

INTERACTIONS BETWEEN SUSPENDED SEDIMENTS, NUTRIENTS AND
FRESHWATER INFLOW IN TEXAS ESTUARIES

A Dissertation

by

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FRESHWATER INFLOW IN TEXAS ESTUARIES

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ABSTRACT

It is important to identify the role of sediments in controlling the concentrations of inorganic nutrients to manage the health of an estuary. The objectives of the present study were to identify the effects of freshwater inflow (FWI) on sediment transport and nutrient supply to estuaries, and the effects of sediments on nutrient supply at sediment-water interface. Field samplings (Chapter II), multivariate modeling approaches (Chapter III), and laboratory experiments (Chapters IV and V) were used to accomplish the research objectives.

Sediments and inorganic nutrients were compared in the Nueces, Guadalupe, and Lavaca-Colorado Estuaries because they have different flow regimes. Variability of suspended solids and nutrients were correlated with FWI in the Guadalupe Estuary but in the Nueces and Lavaca-Colorado Estuaries they were correlated with seasonal differences. Increases in suspended sediments resulted in increased ammonia concentrations in the Guadalupe Estuary, increased phosphorus and silicate concentrations in the Nueces Estuary, and increased silicate concentrations in the Lavaca-Colorado Estuary.

Multivariate modeling was used to analyze water quality data from the three estuaries. FWI was responsible for the increase in inorganic nutrients. Orthophosphate and silicate concentrations were correlated with total suspended solids and chlorophyll-a concentrations.

The sediment-water aerobic layer inorganic nutrients fluxes were identified by conducting laboratory experiments using sediments from the Guadalupe and Nueces Estuaries. Silicate minerals present in the sediments maintain silicate concentrations. Organic matter and

calcium carbonate shells in sediments bind phosphate, and thus, play a role in decreasing phosphate concentrations in the water. The Guadalupe River sediments, when transported to the estuary, can release ammonia at higher concentrations than the river water concentrations. The release of ammonia by organic matter decomposition was lower in the Guadalupe Estuary than in the Nueces Estuary. High FWI in the Guadalupe Estuary may wash away organic matter from sediments and disturb bacterial communities, resulting in lower release of ammonia compared to the Nueces Estuary.

This research demonstrates that sediments, organic matter, and freshwater inflow maintain inorganic nutrient concentrations in estuaries, and hence, may play an important role in the estuarine ecology. Water supply projects trap sediments and divert FWI, thus can alter estuary health.

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CHAPTER I

INTRODUCTION

1.1. Freshwater Inflow

Sediment moves from the watershed to the sea by fluvial transport. Freshwater inflow is the term used to describe when river flow enters a bay or estuary. The freshwater inflow rate from upstream channels to estuaries maintains the functioning of estuary ecosystem components (Kemp et al. 1997; Caffrey 2004; Russell 2006; Montagna et al. 2013). Freshwater in the form of runoff through the river channel maintains nutrient supply and salinity conditions spatially and temporally.

A general conceptual model describes how freshwater inflow (FWI) changes the conditions of an estuary by changing the state of nutrient, salinity and sediment dynamics (Fig. 1.1). The effect of physical forcing in the form of FWI can be seen in biological communities. In Rincon Bayou, Texas, restored FWI increased the number of benthic species diversity, abundance and biomass (Montagna et al. 2002). Similarly benthic responses to altered hydrology have been found in other Texas estuaries (Palmer et al., 2011; Montagna & Kalke 1995; Montagna & Kalke 1992 and Pollack et al. 2009). These studies demonstrate biological resources change with change in freshwater inflow in the estuaries.

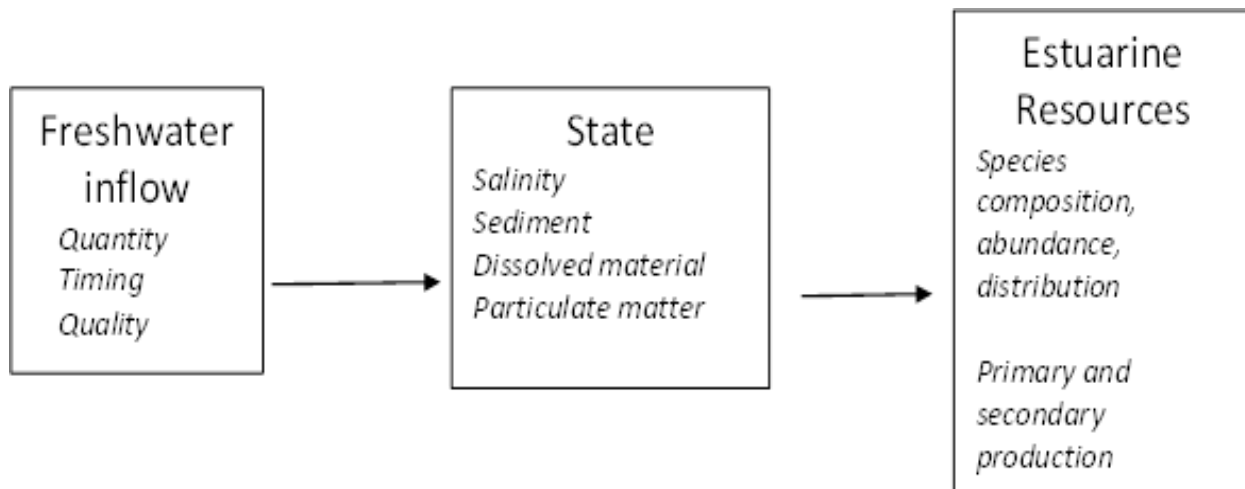


Fig 1.1 Schematic diagram of the effects of freshwater inflow on estuaries. (Alber 2002; SAC 2009; Palmer et al. 2011).

Transported sediments are a reservoir of nutrients, which bond with sediment particles and are released in the water column via various biogeochemical reactions. In a tropical estuary, Saenger & Holmes (1992) demonstrated the low concentration of available nutrients in sediment, which is due to the low sediment nutrient content in the respective watershed soil. Because nutrient levels in the estuary depend in part on the sediment carried to it, sediment transport has an important role in nutrient supply to the system. Thus FWI acts as carrier of sediment and stimulator in changing nutrient conditions of the estuary.

Freshwater inflow is the physical energy that transports matter into estuary systems. An experiment comparing three tropical and temperate estuaries found a strong positive correlation between total suspended solids (TSS) and increases in flow for the tropical estuaries, but no correlations in the temperate estuaries (Eyre and Balls 1999). In the temperate estuaries, they have identified that TSS was mostly related with local resuspension. In addition, Eyre and Ball (1999) also identified TSS concentrations was related with resuspension in all 6 estuaries during dry seasons. In Texas estuaries, inflow and wind driven resuspension events could be important for the increase in TSS concentration. Interestingly in their study of Texas bays using lead isotopes, Powell et al. (2002) has found no correlation between freshwater inflow and change in sediment deposition. So although Texas estuaries are in a subtropical climate zone, they appear to behave like a temperate estuary. The findings of these studies indicate that there are still uncertainties as to the exact relationship between FWI and sediment transport.

While much attention has been focused on biological or water quality change in estuaries as a function of altered freshwater inflow, much less is known about the role of sediments as nutrient carriers, its properties, and its effects in fresh and marine environments. The salinity effects on

the sediment ion exchange capacity can retention and release different positively charged particles to and from the sediments. The salinity in water also affects pH at sediment-water interface that also can affect retention and release of nutrients to/from sediments. To understand the complete change in estuary conditions caused by altered FWI we must study all individual components (i.e., inflow, nutrients, sediments, and salinity) and their interrelated roles.

Presented here is an updated conceptual model of how altered FWI affects biological resources by altering nutrient and sediment dynamics in an estuary (Fig 1.2). As freshwater flows through different climatic, geologic, topographic, and biologic environments, aquatic biogeochemical parameters, such as pH and the concentration of dissolved chemicals, change spatially and temporally. This change would be even more pronounced when freshwater mixes with estuarine saline water. Slight changes in water chemistry might affect ionic charge particles in the transported sediment. Thus, spatial and temporal variation in FWI might affect sediment ionic bonds and ionic charge particles present in the sediment. Also, the strength of ionic bonds in sediment varies with mineral type in the sediment, because of the variation in ionic charge particles associated with different minerals (Quafoku et al. 2004; Sollins et al. 1988). This property of sediment and the transported amount might affect biological resources without affecting the condition or state of the estuary described in Fig 1.2. Different sediment mineralogical composition and the associated variation in nutrient release might favor one plant or animal community over another. Furthermore, the habitat preferred by animal or plant communities might also be different from one another with respect to sediment grain size and mineral composition. This could also change biological resources over time in the ecosystem development process (Fig 1.2). Hence, FWI and sediment might interact together to affect biological resources.

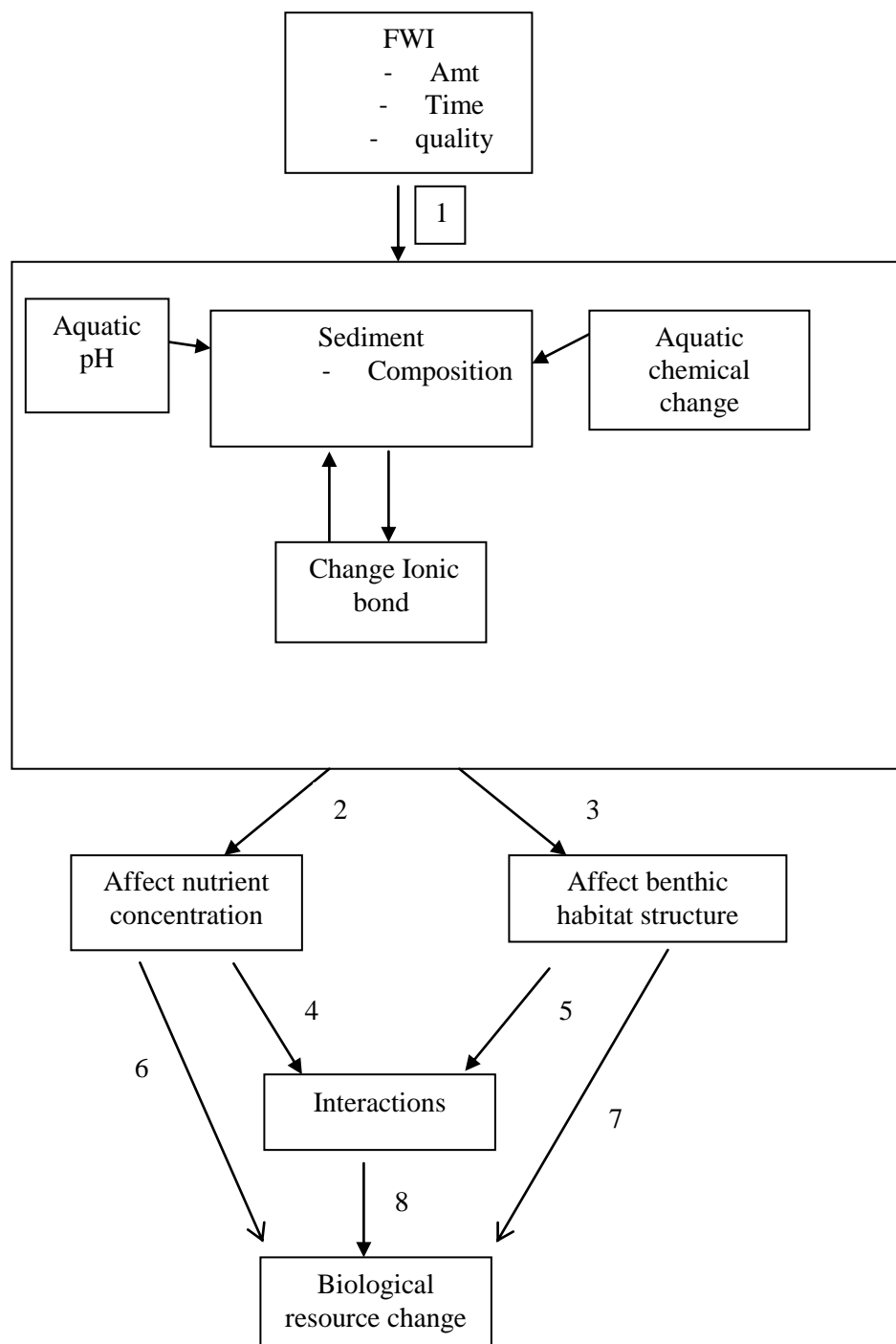


Fig. 1.1 Conceptual model to show role of sediment in changing biological resource of the estuary. Number by the arrow indicate paths.

The goal of the present study was to identify processes and interactions from path 1 to path 2 of the conceptual model shown in Fig. 1.2. In order to accomplish this goal, a field study, laboratory experiments, and multivariate statistical approaches were conducted.

1.2. Altered Inflow

Humans have altered water courses by building dams through time, but the size and number of dams has increased exponentially since the 1940's (MEA 2005). Water flowing through rivers and streams without dams will carry more sediment, thus when deposited in the bay may provide more nutrients. For large rivers it can require approximately 500 km from a dam for natural sediment transport processes to return to that of pre-dam levels (Hudson 1997). Even a small dam, retains large amounts of sediment, thus retaining important nutrients like nitrogen (N), silica (Si) and phosphorus (P). Phosphorus has a low bonding-affinity towards water molecules compared to a high bonding-affinity towards inorganic minerals, which makes phosphorus adhere to the sediment. Thus to transport phosphorus, sediment has to move and this is one of the major reasons for the slow movement of phosphorus compared to nitrogen (Bennett et al 2001). Furthermore, phosphorus in organic rich freshwater-sediment forms a complex with iron and aluminum ions and adheres to sediments. When sediments move to the more saline estuary, phosphorus desorbs due to the decrease of iron and aluminum ions and increase of negatively charged metal oxide ions (Sundareshwor and Morris, 1999). As organic sediment is transported further up in the estuary, it flocculates with more saline water retaining the P-load sediment in the bed (Howarth et al. 1995), thus phosphorus retention in sediment is higher in the middle part of an estuary compared to the confluence point of the river and estuary (Nielsen et al. 2001). From past research findings, we can predict that phosphorus deficiency might be possible

in ocean sediments in those areas where estuarine flow velocity is negligible, because of slow sediment movement.

Nitrate (NO_3) is a form of nitrogen that is water soluble and can flow without the movement of sediment (Stanley, 2002), whereas ammonia (NH_3), another form of nitrogen, desorbs from sediment in the form of ammonium ion (NH_4^+) as freshwater enters into the increased salinity of estuaries (Rysgaard et al 1999; Giblin et al. 2010; Weston et al. 2010; Holmes et al 2000).

Nitrification and denitrification are the two major processes enhanced by aerobic and anaerobic bacteria for nitrogen flux in an aquatic system. Denitrification of nitrogen occurs in anaerobic conditions, and the accumulation of fine sediments caused by negligible flow rates behind dams favors anaerobic conditions because of the gradual decrease in porosity in the finer sediments (Garcia-Ruiz et al 1998). Past researchers have found an inhibition effect of salinity on nitrification and denitrification (Rysgaard et al. 1999; Seitzinger et al. 1991), however there is no evidence of significant regulatory effects of salinity on denitrification in Duoro River estuary (Magalhaes et al. 2005). Thus, change in FWI due to dams or diversions could affect structural and functional change in the estuary's environment over space and time.

Increase in salinity increases cations such as Na^+ and Mg^{2+} , which in turns compete with NH_4^+ to bond with negative charged particles, and this causes NH_4^+ release into the water column (Seitzinger et al 1991; Rysgaard et al 1999; Rosenfeld 1979; Grasshoff et al. 1983). Saline estuary water has anions like Cl^- , which then pair with free NH_4^+ . This ion pairing is the reason NH_4^+ is not being adsorbed in estuarine sediment compared to freshwater sediment (Gardner et al. 1991). Salinity driven desorption of NH_4^+ ion was found to be important in the Parker River estuary, and for maintaining primary productivity during low-flow or during the

summer season (Holmes et al 2000; Hopkinson et al. 1999). Ion desorption might be an important driver of N flux in other estuaries as well.

Sediment carried by freshwater inflow is the primary source of dissolved silica in estuaries (Humborg et al. 2000). Effects of dams on Si would be more significant compared to nitrogen and phosphorus, because N and P demand could be supplemented by agricultural runoff entering the bay from regions behind the dam (Papush and Danielson 2006; Humborg et al. 2000; Perran et al 2010). Dissolved silica, which is important in maintaining primary productivity of aquatic ecosystems, is an essential nutrient for the growth of diatoms (Turner 2001), tends to deplete in the water column because of eutrophication (Turner 2001; Papush and Danielson 2006). Hence diversions or dams might have a significant role in controlling dissolved silica in estuaries.

1.3. Sediment Transport and Ecosystem Response

Sediments trapped are less likely to be retained for long term but undergo resuspension and deposition. Sediment transport in water is a function of resuspension and deposition with discharge rate a controlling factor. Resuspension in aquatic ecosystems has a role in the transfer, balance and release of nutrient load into the water column (Wainright 1990). Resuspension can meet 94% of N and 83% of P requirements for phytoplankton species (Cowan et al. 1996). A strong triggering mechanism, such as a storm, could stimulate up to 200% of phytoplankton productivity by increasing nutrients in the water column by disturbing the top 1 mm of bottom sediments in the Gulf of Mexico continental shelf and Texas bays (Fanning et al. 1982; Madsen et al. 2001). Different factors such as vegetation cover, wind speed, wave action, sediment particle size and texture, and water residence time control deposition of sediments from the water column to wetlands (Settlemyer and Gardner 1977; Boto and Patrick, 1979; Gleason et al. 1979;

Kamp-Nielson, 1983; Ward 1985). Deposited organic matter is the source of nutrients only if the rate of resuspension is faster than the rate of deposition (Schulz et al 2003). The combined effects of deposition and resuspension are critical in maintaining nutrient balance.

Nutrient load contributed from sediment loading was high in the Mississippi River Basin (Miao et al. 2006). Sediments release nutrients, such as nitrogen and phosphorus, when they enter an estuary, and different rooted macrophytes depend on this sediment supply of nutrients (Carigan 1985). A high volume of freshwater inflow carries lots of sediment, and thus should load more nutrients. River systems have more nutrients than river-estuary and lagoons systems (Palmer et al. 2011), which might be because of the continuous movement of sediments resulting the release of nutrients in the water column. Another recent study carried out in the east coast of India concluded that increased amount of sediments due to tsunamis does increase the concentration of nitrate, phosphate and silicate significantly, but could have a negative effect on phytoplankton population because of high turbidity (Satpathy 2010). Accumulation of sediment in the bed could retain nutrients so that it is not getting into the water columns.

Abrupt changes in sedimentation are responsible in changing biodiversity and succession of coastal ecosystem (Satpathy 2010). Abrupt changes like flood pulses can flush sediment because of the high volume discharge (Bayley 2009), which could decrease the nutrient content by removing top layer organic rich fine sediments and increase it where it deposits. Sand composition of sediment sometimes also acts as an abrasive agent destroying benthic components (Bayley 2009).

Nutrients are also retained in benthic biomass due to sediment and benthic organism interaction (Josefson and Rasmussen 2000). Previous work suggests that filter feeding organisms

in estuaries retain nutrients either by absorbing nutrients in their body tissue or by recycling faster than flushing of nutrients carried by freshwater. Benthic microalgae, are also responsible for nutrient cycling (Spears et al. 2008) and have a role in reducing release of nutrient such as P, N and SiO₂ from sediments (Jansson 1980; Kelderman et al. 1988; Jarvie et al. 2002).

Microphytobenthos and phytoplankton assimilate most of the watershed nitrogen present in the upper reaches of estuaries. The assimilated nitrogen in the cells of phytoplanktons and benthic microalgae are deposited; and suspended sediments can be the source of N to the lower reaches of estuaries when released into the benthic sediment by denitrification or decay (Holmes et al. 2000).

Change in total suspended solid (TSS) and chlorophyll a (Chl-a) is also a possible effect of freshwater inflow and sediment transport. Substantial evidence links human activities along the land-sea continuum to increased stressors, such as nutrients, Chl-a, and TSS (Cloern, 2001; Bricker et al., 2007). Spatial and temporal variability of watershed discharge of stressors affect variation in ecological regimes among estuaries and temporal variation within estuaries. Much of this variability is driven by differences in land use and land cover and variable flow regimes. Thus, the present study has measured fluctuation of sediments, nutrients, and chl-a to infer water quality and biological changes in shallow estuaries. The study has also helped in establishing water quality standards based on three indicators i.e., TSS, CHLA and inorganic nutrients for the three Texas bays.

1.4. Rationale and Purpose

The main purpose of this study is to identify the role of sediment supply in maintaining nutrients in the Nueces, Lavaca-Colorado, and Guadalupe Estuaries. Sediment supply and its

composition are transported by freshwater inflow and pivotal in altering nutrients in the estuaries. Developing this new scientific understanding increases our knowledge about the relationship between flow and estuary condition in general, and enhance our ability to manage the health of estuaries with respect to FWI.

To determine the nature of change in ecosystem health caused by sediment mineral composition, grain, and amount, the following major questions will be answered:

1. How does sediment supply and composition affect functioning of ecosystems in receiving waters?
2. Does altered freshwater inflow to an estuary result in altered nutrient loadings?

In order to answer the research questions the following were the major study objectives:

- To identify effect of freshwater inflow in relation to the change in TSS, organic matter, and inorganic nutrient concentration.
- To identify fluxes of inorganic nutrient at sediment-water aerobic layers.

1.5. Study Area

Lavaca-Colorado (LC), Guadalupe (GE) and Nueces (NC) Estuaries were the three estuaries chosen to answer the research questions (Fig 1.3). These three estuaries, in Texas, lie in the climatic gradient with the Lavaca-Colorado Estuary receiving more inflow than the Guadalupe and Nueces Estuaries (Montagna et al. 2013). Thus, the spatial and temporal variability in sediment and nutrients transport vary as well.

1.6. Study Approach

Four linked experiments were performed to achieve the goal of this study. The relationship between TSS and inorganic nutrients were studied in the Lavaca-Colorado, Guadalupe, and Nueces Estuary using field data (Chapter 2). Direct and indirect effects of inflow on the fluctuation of inorganic nutrients in the three estuaries were studied using multivariate approaches (Chapter 3). Orthophosphate and silicate fluxes at the sediment-water interface were studied in the laboratory settings, to identify the effect of organic matter and sediment mineral content (Chapter 4). The difference between inorganic nitrogen fluxes were studied in the laboratory settings from the sediments of the Guadalupe and Nueces Estuary (Chapter 5). In the sixth chapter, I have concluded with a summary of the findings of my dissertation.

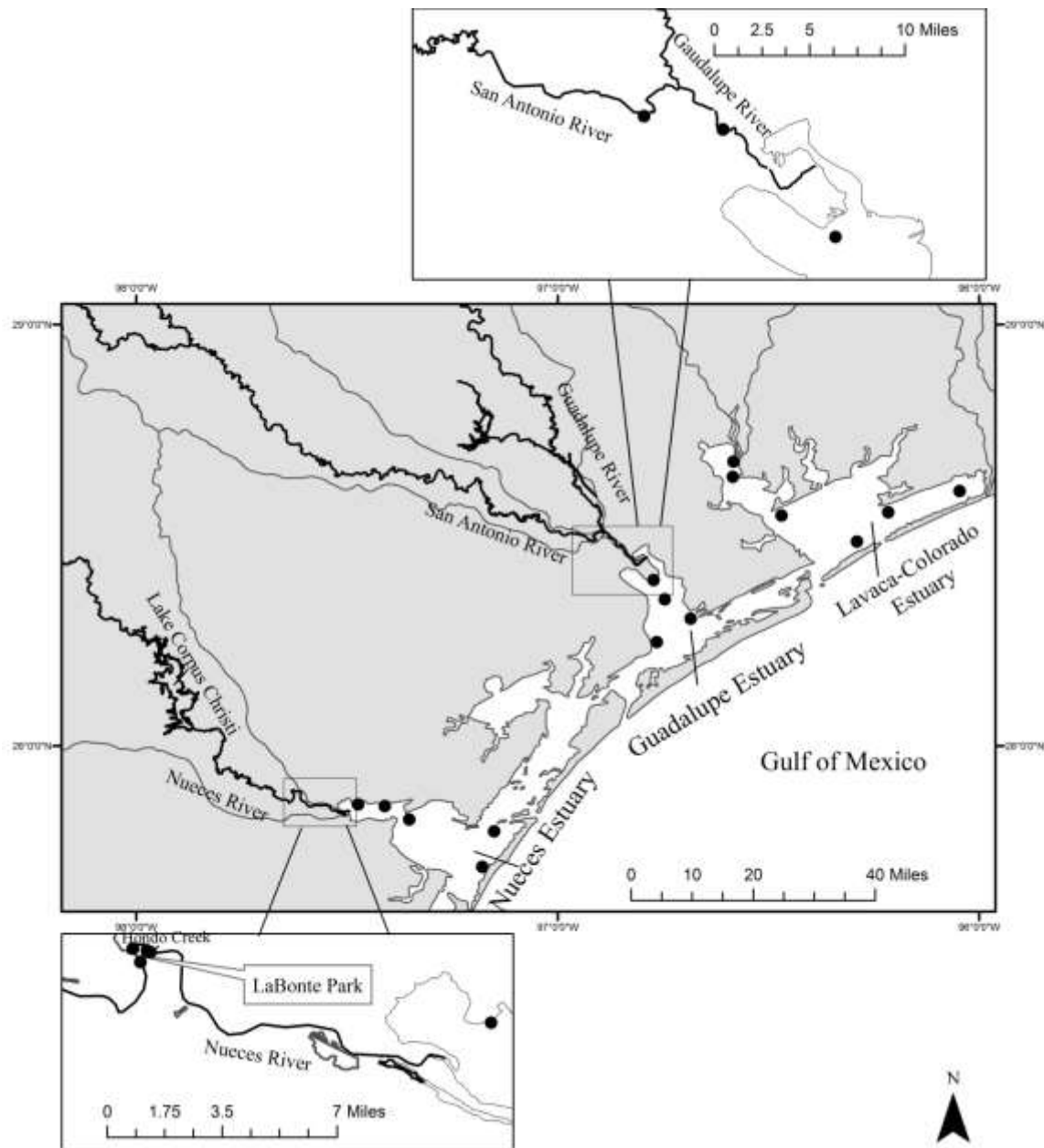


Fig. 1.3 Map of study sites with sampling stations

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CHAPTER II

RELATIONSHIP BETWEEN TOTAL SUSPENDED SOLID AND INORGANIC NUTRIENTS IN SOUTH TEXAS GULF COAST ESTUARIES

Abstract

The purpose of the current study was to identify the role of total suspended solid (TSS) in contributing to surface water inorganic nutrient concentrations. Three South Texas coastal estuaries (Nueces, Guadalupe, and Lavaca-Colorado) with different hydrologic flow regimes were compared. Stations were selected in each estuary along the gradient between river inflow and the Gulf of Mexico. Phytoplankton and inorganic detrital constituents of sediments were considered to be TSS. The Lavaca-Colorado Estuaries had seasonal changes in TSS, silicate, and orthophosphate. The Guadalupe and Nueces Estuaries had inflow effects on TSS and NH_3 . In all three estuaries combined data set, ammonia ($r^2=0.4$) had a weak positive correlation with TSS, while silicate ($r^2=0.7$) and orthophosphate ($r^2=0.6$) had a strong positive correlation with chlorophyll-a. Nitrite+nitrate, ammonia, orthophosphate and silicate concentrations were the highest at 180 mg/L of TSS. Ammonia was positively correlated with TSS in the Guadalupe and Nueces Estuaries. Orthophosphate concentration was significantly related with TSS concentrations only in the Nueces Estuary. The negative correlation of ammonia with salinity in all the three estuaries and the negative correlation of nitrite+nitrate with salinity in the Guadalupe Estuary indicate amount of inflow controls nitrogen in the three estuaries. This study demonstrates phytoplankton and TSS were directly related to the change in concentration of silicate, orthophosphate and ammonia, which implies that reduced inflows that cause reduced sediment load would reduce dissolved inorganic nutrient to the estuaries. Furthermore, high TSS

concentrations during frontal and wind events are important in supplying dissolved inorganic nutrients in the estuaries.

Key Words: total suspended solids; TSS; inorganic nutrients; estuary; freshwater inflow; sediment load

2.1. Introduction

Freshwater inflow to estuaries is important to maintain estuarine health and productivity (Montagna et al. 2002; Montagna et al. 2013a). While much attention has been focused on biological or water quality changes in estuaries as a function of altered freshwater inflow, much less is known about the role of total suspended solids (TSS) as nutrient carriers. In South Texas estuaries, past studies have linked changes in nutrient loading to freshwater inflow (Brock 2001; Montagna and Li 2010), changes in nutrient concentration to salinity (Pollack et al. 2009; Russell et al. 2006) and changes in nutrient concentration to animal types (Riera et al. 2000; Palmer et al. 2011). However, the link between TSS and nutrient concentration is less well studied. The TSS can have direct and indirect effects on the primary productivity of an estuary by directly affecting photosynthesis by blocking sun-light, and indirectly by affecting water chemistry by releasing and adsorbing inorganic nutrients.

In shallow estuaries, suspended sediments and bed sediments have significant effects on the dissolved inorganic nutrient concentration. Permanently suspended particulate matter and resuspendable particulate matter adsorb and release different forms of nitrogen in the water column (Ding and Henrichs 2002; Tappin et al. 2010). The variation in adsorption partition coefficients affects protein adsorption in different types of clay minerals, which in turn affects nitrogen release from the sediment (Ding and Henrichs 2002). In the Ogeechee River Estuary, TSS that remained mostly in the suspended fraction was high in particulate organic nitrogen (Alber 2000). A lab experiment on high and low solid to solution ratio of Laguna Madre estuary sediments showed release of NH_4^+ from resuspended sediments (Morin and Morse 1999).

Phosphorus in organic rich freshwater sediments forms a complex with iron and aluminum ions and adsorbs to sediments. As the organic rich freshwater sediments move into the more saline estuary, phosphorus desorbs due to the increase in electrolytes and negatively charged metal oxides (Sundareshwor and Moris 1999). Resuspension is important because phosphorus released from resuspended sediments was 20-30 times greater than from undisturbed lake sediments (Sondergaard et al. 1992). Phosphorus has a tendency to adsorb and bond with calcium carbonate rich sediments (McGlathery et al. 1994), and release during resuspension (Spagnoli and Bergamini 1997).

Sediments carried by freshwater inflow are the primary source of dissolved silica in estuaries (Humborg et al. 2000). Silicate minerals sedimented in estuaries can control dissolved silicate concentration (Rickert 2000; Rickert et al. 2001). In the laboratory experiments, release of silicate concentration from the sediments containing silicate minerals of Guadalupe, Lavaca-Colorado and Nueces Estuaries indicates the sediments are maintaining silicate concentration (Paudel unpublished). Silicate is required by diatoms and diatoms can recycle silicate in the estuaries (Conley 1992).

The purpose of the present study is to identify relationships between TSS and inorganic nutrients. The hypotheses tested were: (1) there was no correlation between TSS and inorganic nutrient concentrations, and (2) there were no significant effects of TSS on inorganic nutrients concentration. In the present study, phytoplankton (estimated by chlorophyll-a concentration) and inorganic detrital constituents of sediments were considered as TSS.

2.2. Methods

2.2.1. Study sites and sampling design

Three South Texas estuaries, Lavaca-Colorado (LC), Guadalupe (GE) and Nueces (NC), (Fig. 2.1) were studied to examine the relationship between TSS and inorganic nutrients. The estuaries have similar geographic structure, but have different inflow regimes (Montagna et al., 2013a; Montagna and Li, 2010). River inflow decreases towards the southwest of LC estuary. Average inflow for LC, GE and NC estuaries are $3679 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$, $2677 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$, and $348 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ respectively (Montagna et al. 2013a).

To study TSS and inorganic nutrient concentrations six, four and five stations in the LC, GE and NC Estuaries respectively were sampled. The stations were located along salinity gradients from the major freshwater sources to the tidal inlets of the Gulf of Mexico. Stations A, B and F were closer to the river mouth in the estuaries compared to stations C, D, and E, which were closer to the Gulf of Mexico (Fig. 2.1). The stations closer to freshwater source were called “near” stations and those further from freshwater source were called “far” stations.

The stations were sampled quarterly from April 2011 to Oct 2013 in all three estuaries to collect water samples for TSS, chlorophyll-a and inorganic nutrients. Dissolved oxygen (DO), pH, temperature, salinity and conductivity were measured at each sampling event using an YSI Hydro lab Sonde.

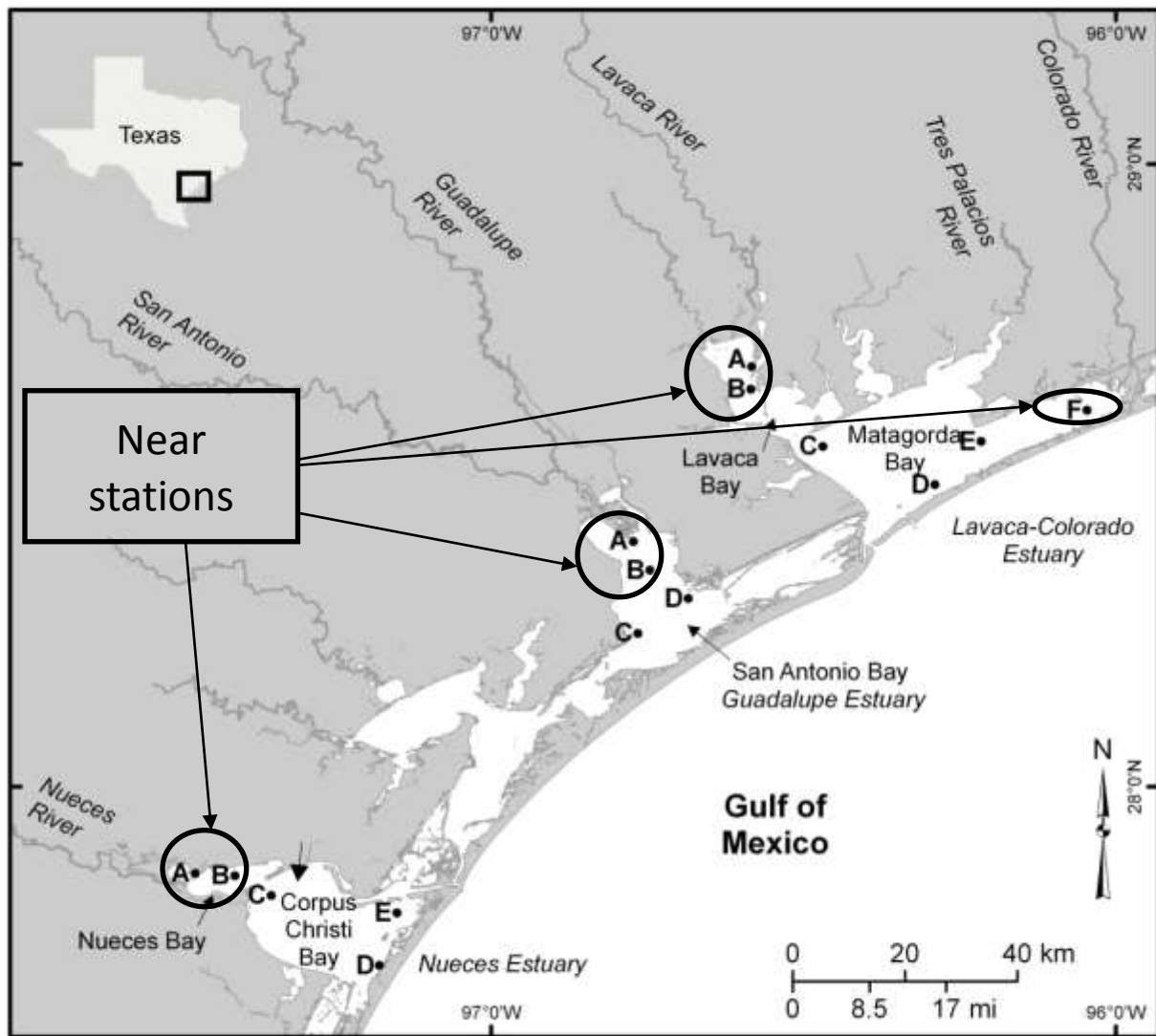


Fig. 2.1 Maps showing estuaries and sampling stations present in each estuary

2.2.2. Total Suspended Solid (TSS)

Surface water samples were collected by hand using 500 ml brown Nalgene bottles and bottom water, i.e. 20 cm above sediment, were collected using Van Dorn sampler. Two replicate water samples were taken at each station. Water samples were kept on ice after collection and filtered within 24 hours of collection. Filtered sediment samples were dried and weighed to determine TSS.

2.2.3. Chlorophyll-a and Inorganic Nutrients

Water samples were filtered on site and then stored frozen. In the lab, chlorophyll-a was extracted overnight using methanol. Turner Design Trilogy fluorometer was used to determine Chlorophyll-a concentration using a methanol extract method (Krauk et al. 2006). Analysis was performed within 12 to 16 hours of methanol addition.

Nutrient samples were filtered on site using 0.45 μm polycarbonate filter paper and kept on ice. All nutrient samples were stored frozen until analysis and were processed for inorganic nutrient analysis within two weeks. Nutrient analysis was conducted using the O.I. Analytical Flow Solution IV® (FS IV®) auto analyzer that combines both segmented flow analysis and flow injection analysis techniques with computer controlled sample selection and peak processing.

Nutrient chemistries are as specified by the manufacturer. Manufacturer recommended applicable range of method detection limit (MDL) are 0.1-10 $\mu\text{mol/L}$, 0.02-10 $\mu\text{mol/L}$, 0.35-35 $\mu\text{mol/L}$, and 0.02-40 $\mu\text{mol/L}$ for ammonia (NH_3), orthophosphate (o-PO_4), silicate (SiO_4), and nitrite+nitrate (NO_{2+3}). Matrix matching between the carrier, standards and the sample matrix

minimizes refractive index effects on absorbance, which are mainly caused by salinity. Matrix matching is particularly important for nitrogen (N) chemistries and requires the use of low nutrient seawater (LNSW) to accurately detect low (μmol) levels of N in samples. For both orthophosphate and silicate chemistries, artificial seawater is adequate for the analysis. The typical lowest concentration minimum reportable levels (LCMRL) are: nitrate+nitrite (0.25-10.0 μmol ; O.I. Analytical method 15040908, OIA 2008), silicate (10.0-300.0 μmol ; O.I. Analytical method 15061001, OAI 2001a), and ammonia (0.25-10.0 μmol ; O.I. Analytical method 15031107, OIA 2007). The orthophosphate method has a LCMRL of 0.10-10.0 μmol (Perstorp Analytical method 000589, OIA 2001b), but is a modification of the Alpkem chemistries method (Alpkem 1993). In the present study LCMRL was used to prepare standard curve for the analyses.

2.2.4. Statistical Analysis

Multivariate analysis of variance (MANOVA) was performed to analyze relationships between inorganic nutrients, and TSS along near and far stations. All the data were log transformed in order to get normal distribution of residuals. Analysis was done by individual estuaries and by merging water quality data from all three estuaries. The average of the near versus far stations were calculated for each estuary to identify the TSS and inorganic nutrient transport along the estuary salinity gradient. Pearson's correlation was performed between TSS and inorganic nutrient concentrations in all the three estuaries to identify the link between these variables. SAS version 9.2 was used for the statistical analysis. MANOVA was performed using PROC GLM procedure, Pearson's correlation was performed using PROC CORR procedure, and all plots were created using PROC GPLOT and SAS ODS graphics designer. SAS contour plot

was used to identify the relationship between TSS, chlorophyll-a, and inorganic nutrients. SAS ODS graphics gradient contour type with three color ramp shows the continuous response of z variables (inorganic nutrient concentration) with the change in x (TSS) and y (chlorophyll-a) variables. Principal component analysis (PCA) was performed to analyze the relationship between TSS, inorganic nutrients and fore mentioned water quality variables. Before the analysis data were standardized using PROC STANDARD. PROC FACTOR procedure was used to perform principal component analysis (Carr et al., 2000; Long et al., 2003). Axis rotation was done by VARIMAX rotation.

2.3. Results

2.3.1. Existing Inorganic nutrients and suspended solid components

Ammonia (NH_3) was below detection limit of $0.25\mu\text{mol/L}$ in the months of July 2011, October 2011 and January 2012 in the Nueces (NC) Estuary, and in the month of October 2011 in the Guadalupe (GE) and Lavaca-Colorado (LC) Estuaries (Fig. 2.2). In the NC and LC Estuaries concentrations ranged from below detection limit to $5.07\mu\text{mol/L}$ and $6.15\mu\text{mol/L}$ respectively, but most of the times were equal or less than $1\mu\text{mol/L}$. In April 2012 and July 2012, LC estuary ammonia concentration peaked at greater than $3\mu\text{mol/L}$, and then dropped close to $1\mu\text{mol/L}$ afterward. In GE estuary concentrations were below detection limit to $4.90\mu\text{mol/L}$, with most of the values falling between 1 and $3\mu\text{mol/L}$. In all the three estuaries, ammonia concentrations were not significantly different between near and far stations, except on high peak inflow events (Table 2.1).

In the GE Estuary, nitrite+nitrate (NO_{2+3}) concentration was significantly different between near and far stations but not in the NC and LC estuaries (Table 2.1). In the GE Estuary, most of the higher concentrations were from near stations. NO_{2+3} ranged from below detection limit ($0.25\mu\text{mol/L}$) to $1.80\mu\text{mol/L}$ in NC, $27.8\mu\text{mol/L}$ in GE and $11.265\mu\text{mol/L}$ in LC. Highest GE NO_{2+3} concentration of $27.8\mu\text{mol/L}$ was during the month of April 2012. Most of the samplings were accompanied by low, i.e. less than $1\mu\text{mol/L}$, NO_{2+3} concentration in all three estuaries (Fig. 2.2).

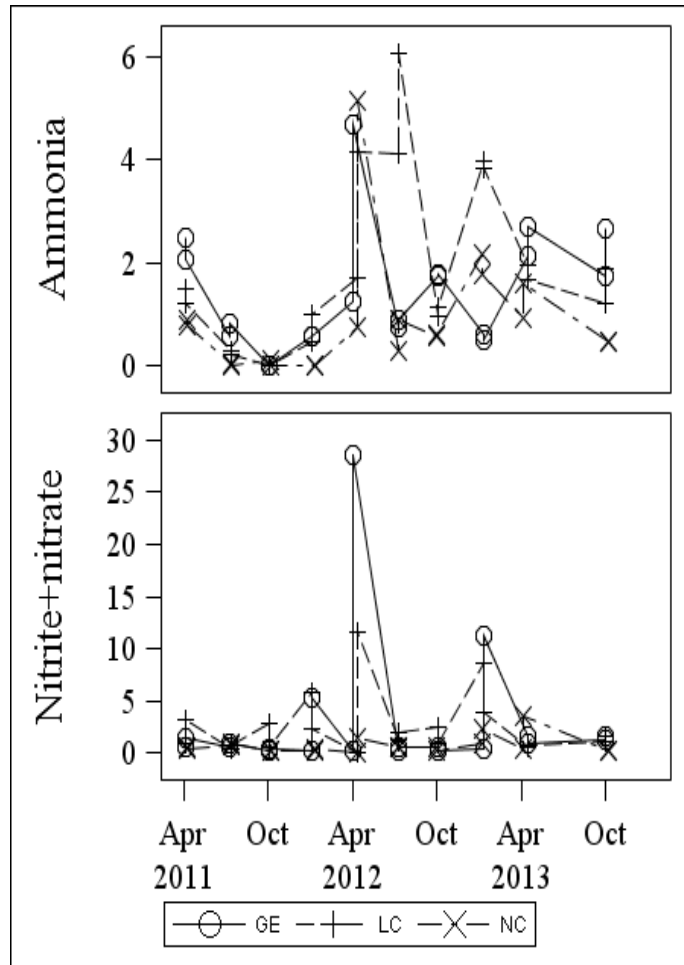


Fig. 2.2 Average ammonia and nitrite+nitrate concentration in the three estuaries. Higher values respective to each date were from near stations. Ammonia and nitrite+nitrate were measured in $\mu\text{mol/L}$. GE= Guadalupe Estuary, LC= Lavaca-Colorado Estuary, NC= Nueces Estuary

Orthophosphate (o-PO_4) concentration was significantly different between near and far stations in NC and LC but not in GE (Table 2.1). The highest o-PO_4 concentration was identified in the month of October 2012 in all the three estuaries (Fig. 2.3). o-PO_4 ranged from below detection limit ($0.1 \mu\text{mol/L}$) to $1.76 \mu\text{mol/L}$ in NC, 0.15 to $3.03 \mu\text{mol/L}$ in GE, and below detection limit to $1.30 \mu\text{mol/L}$ in LC estuaries. Far stations o-PO_4 concentration was less than $0.5 \mu\text{mol/L}$ in NC. Near stations in the LC Estuary showed high orthophosphate concentration compared to far stations.

In January 2012 silicate concentration was the lowest in all three estuaries. Silicate concentration was highest in October 2012 in the GE and LC Estuaries, whereas July 2012 was the highest silicate concentration month for the NC Estuaries (Fig. 2.3). Silicate (SiO_4) concentrations ranged from below detection limit ($10 \mu\text{mol/L}$) to $135.94 \mu\text{mol/L}$ in NC, $206.21 \mu\text{mol/L}$ in GE, and $120.31 \mu\text{mol/L}$ in LC estuaries. In the NC Estuary, silicate concentration was significantly different between near and far stations but not in the GE and LC Estuaries (Table 2.1). Most of the time far stations silicate concentrations were between 15 and $45 \mu\text{mol/L}$ in the NC and LC Estuaries, in comparison far stations concentrations in the GE Estuary were greater than $80 \mu\text{mol/L}$.

Table 2.1 P-value to determine if different variables are significantly different between near and far stations of Guadalupe Estuary (GE), Lavaca-Colorado Estuary (LC), and Nueces Estuary (NC).

Variable	GE	Test for near Vs far (p-value)	
		LC	NC
TSS	0.1665	0.0179*	0.0002*
NH ₃	0.4034	0.2145	0.0660
NO ₂₊₃	0.0042*	0.3433	0.1067
SiO ₄	0.4363	0.0937	0.0143*
o-PO ₄	0.3425	0.0079*	<0.0001*
Chl-a	0.0007*	0.0177*	0.2005

Stations close to river were named near and those far were named far stations.

* denotes significant value

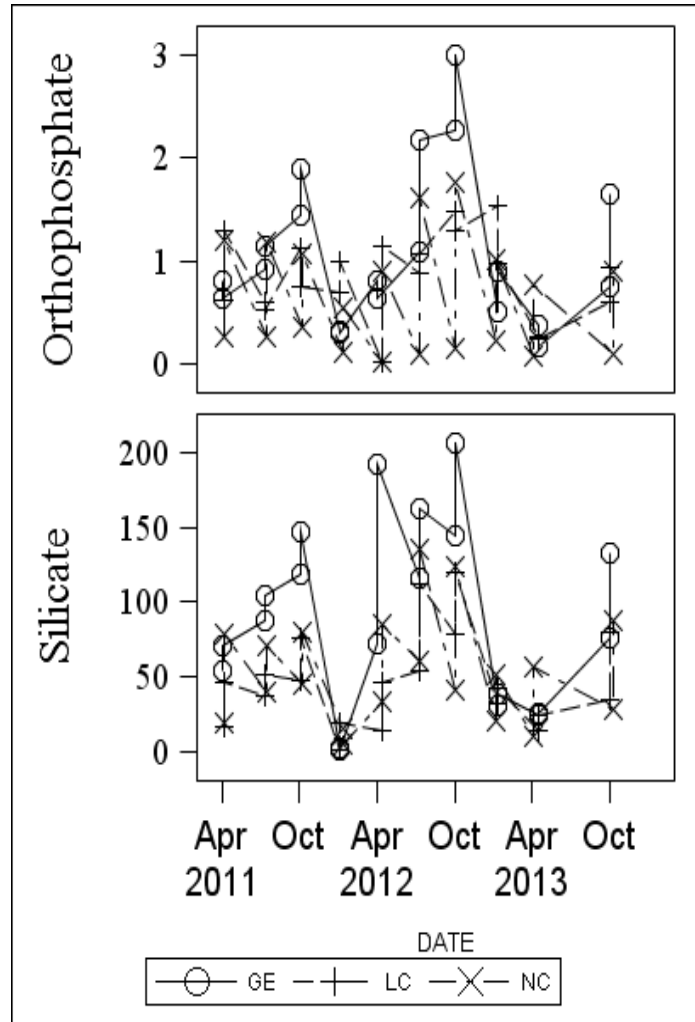


Fig. 2.3. Average orthophosphate and silicate concentration in the three estuaries. Higher values respective to each date were from near stations. Silicate and orthophosphate were measured in $\mu\text{mol/L}$. GE= Guadalupe Estuary, LC= Lavaca-Colorado Estuary, NC= Nueces Estuary

The highest TSS months for the NC estuary were April 2011 and April 2012, whereas for GE and LC estuaries were April 2012 and October 2011 respectively (Fig. 2.4). The highest TSS concentration identified in the cold front events, windy days (>20 miles/hr), and peak flow events. TSS concentrations were significantly different between near and far stations in NC and LC but not in GE (Table 2.1). TSS ranged from 16.59 mg/L to 249.31 mg/L, 17.16 to 182.88 mg/L and 16.48 to 80.24 mg/L in NC, GE and LC estuaries respectively.

In October 2012 chlorophyll-a concentration was the highest in the GE and NC Estuaries, whereas in October 2013 chlorophyll-a concentration was the highest in the LC Estuary (Fig. 2.4). Chlorophyll-a (chl-a) ranged from 0.62 to 20.98 in NC, 2.37 to 29.20 in GE and 2.25 to 15.23 µg/l in LC. Except NC, chlorophyll-a concentrations were significantly different between near and far stations (Table 2.1). In the LC estuary, stations closer to the Colorado River showed more chlorophyll-a in most of the sampling quarters. In the NC estuary, most of the time far stations had low chlorophyll-a concentrations, except in the months of April 2012 and July 2012, when chlorophyll-a was even higher than near stations.

Throughout the sampling period salinity ranged from 31.24 to 45.15 ppt in NC, 1.9 to 37.19 ppt in GE, and 7.9 to 40.31 ppt in LC estuaries. Oct 2011 was the highest saline month in the three estuaries.

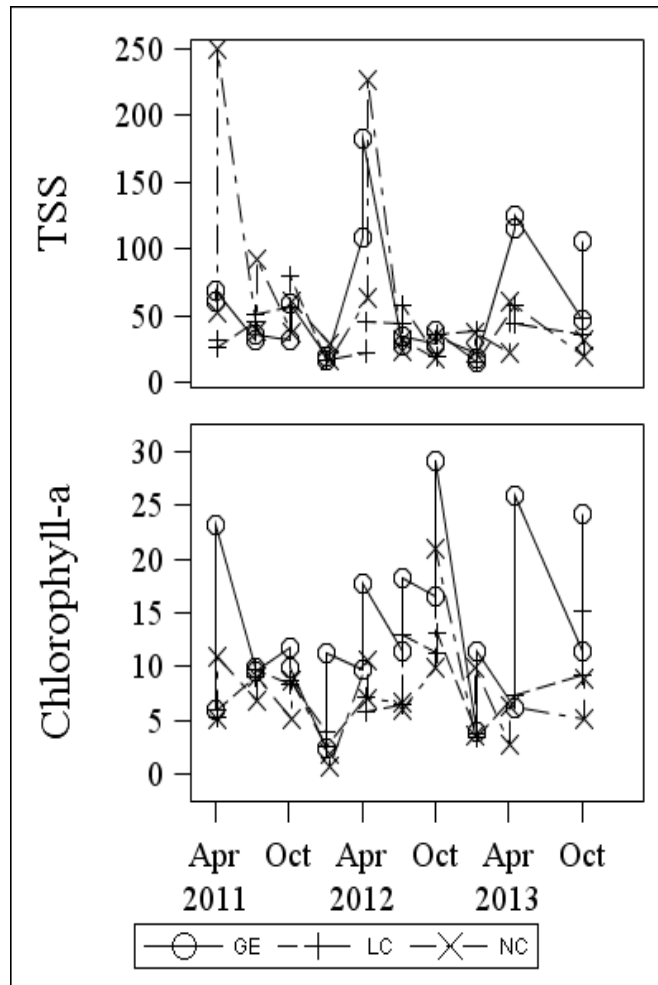


Fig. 2.4. Average TSS and chlorophyll-a concentration in the three estuaries. Higher values respective to each date were from near stations, except in January 2013 and April 2013 average TSS in the LC estuary was higher in far stations. Similarly, in NC April and July 2012 chlorophyll-a was higher in far stations. TSS was measured in mg/L and chlorophyll-a was measured in $\mu\text{g/L}$. GE= Guadalupe Estuary, LC= Lavaca-Colorado Estuary, NC= Nueces Estuary

2.3.2. Relation between Total Suspended Solids and Inorganic Nutrients

NO_{2+3} concentration was identified to be neither increased nor decreased until 125 mg/L of TSS. However, NO_{2+3} concentrations increased from 125 mg/L to 180 mg/L of TSS. NO_{2+3} decreased even if TSS increased beyond 180 mg/L. NO_{2+3} concentration was not related with chlorophyll-a (Fig. 2.5a). When TSS was less than 50 mg/L, feeble increase in NH_3 concentration was identified with the increase in chlorophyll-a concentration. Similar to NO_{2+3} , NH_3 increased with TSS between 100 mg/L to 180 mg/L (Fig. 2.5b).

o-PO_4 increased with chlorophyll-a when TSS was less than 50 mg/L. o-PO_4 decreased between 50 to 150 mg/L of TSS. o-PO_4 increased after 150 mg/L of TSS (Fig. 2.5c). Similar to o-PO_4 , silicate increased with chlorophyll-a when TSS was less than 50 mg/L. SiO_4 concentration increased as TSS increased beyond 150 mg/L, the highest SiO_4 concentration was identified when TSS was 180 mg/L (Fig. 2.5d).

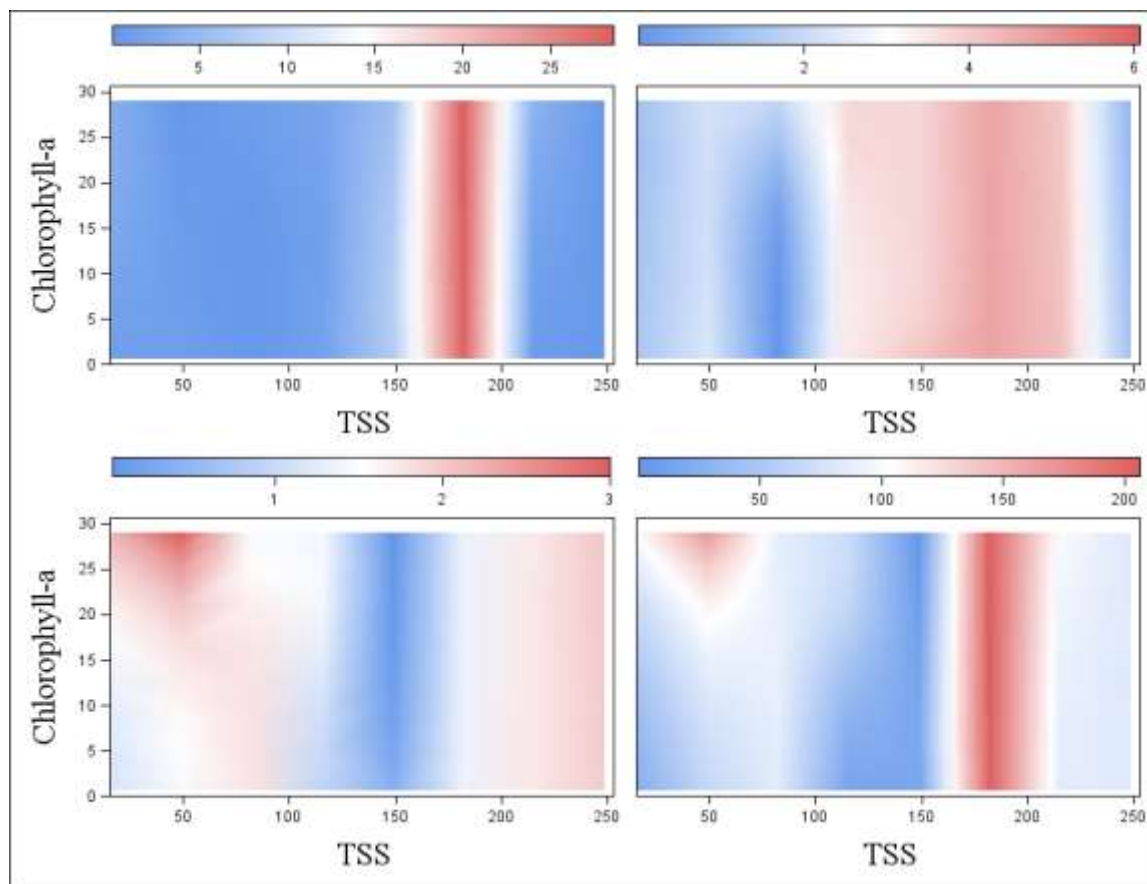


Fig. 2.3 Inorganic nutrients concentration along the gradients of TSS and chlorophyll-a concentration using all the three estuaries combined data set. Color gradients indicate concentration of inorganic nutrients: (a) Nitrite+Nitrate concentration (b) Ammonia concentration (c) orthophosphate concentration (d) silicate concentration. Color gradient legend is placed on the top of each graph.

First three factors explained 82.43% of variation using the Guadalupe Estuary data set. The first and second principal components (PC1 and PC2) explained 45.06% and 23.39% of variation (Fig. 2.6a). PC1 has the highest positive values for TSS, NH_3 , and NO_{2+3} , whereas the highest negative values for salinity. PC2 has the highest positive values for DO and highest negative values for temperature.

First three factors explained 80.9% of variation using the Lavaca-Colorado Estuary data set. The first and second principal components (PC1 and PC2) in Lavaca-Colorado Estuary data set explained 45.09% and 22.15% of variation (Fig. 2.6b). PC1 has the highest positive values for temperature and the highest negative values for DO and secchi. PC2 has the highest positive value for ammonia and the highest negative value for salinity.

First three factors explained 78.15% of variation using the Nueces Estuary data set. The first and second principal components (PC1 and PC2) in Nueces Estuary data set explained 39.91% and 24.78% of variation (Fig. 2.6c). PC1 has the highest positive values for SiO_4 and o-PO_4 , whereas the highest negative values for secchi. PC2 has the highest positive value for DO and the highest negative value for temperature.

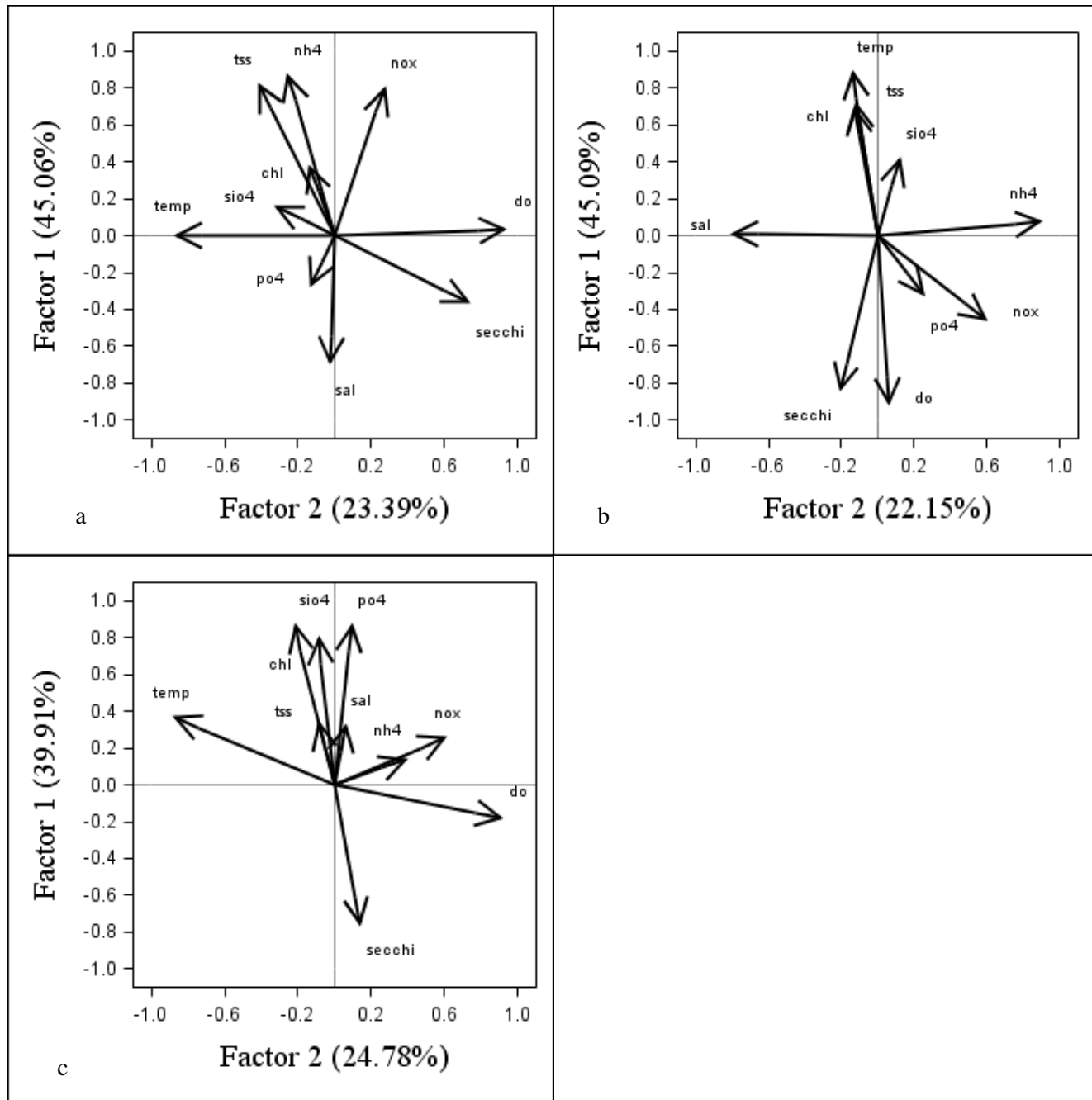


Fig. 2.6. Rotated factor patterns obtained from Principal component Analysis (PCA) using variable loadings for water quality data of the three estuaries. (a) Guadalupe Estuary. (b) Lavaca-Colorado Estuary. (c) Nueces Estuary.

2.3.3. Result of Pearson correlation analysis

In all three estuaries combined data set NH_3 was weakly correlated with TSS (r^2 of 0.4 with NH_3). In addition, SiO_4 and o-PO_4 were strongly positively correlated with chlorophyll-a in the combined data set (Table 2.2). o-PO_4 concentration was positively correlated with chlorophyll-a and TSS in the Nueces Estuaries, whereas only with chlorophyll-a in the Lavaca-Colorado and Guadalupe Estuaries. SiO_4 concentration was positively correlated with chlorophyll-a and TSS in all the three estuaries. NH_3 concentration was positively correlated with TSS in the Nueces and Guadalupe Estuaries, whereas NO_{2+3} concentration was positively correlated with TSS in the Guadalupe Estuary. NH_3 and NO_{2+3} concentrations in the Lavaca-Colorado Estuary were not correlated with TSS (Table 2.3).

Table 2.2 Correlation between inorganic nutrients, TSS and chlorophyll-a (chl-a) in all the three estuaries combined data set. Values are Pearson's coefficient.

	SiO ₄	o-PO ₄	NH ₃	NO ₂₊₃
TSS				
R ²	0.25	0.03	0.4	0.21
P	0.0501	0.79	0.004	0.065
Chl-a				
R ²	0.66	0.50	0.15	0.08
p	<0.0001	<0.0001	0.22	0.52

Table 2.3 Correlation between inorganic nutrients and water quality variables in the Guadalupe, Lavaca-Colorado and Nueces Estuaries. r = Pearson's correlation coefficient and p = estimated probability of rejecting the null hypothesis.

		Nutrients	TSS	Chlorophyll- a	Salinity	
Nueces Estuary	SiO ₄		0.26*	0.57*	0.04	r
			0.03	<0.0001	0.69	p
	o-PO ₄		0.32*	0.45*	0.02	r
			0.007	<0.0001	0.88	p
	NH ₄		0.62*	0.18	-0.32*	r
			<0.0001	0.14	0.007	p
Guadalupe Estuary	SiO ₄		0.16	0.04	-0.048	r
			0.19	0.73	0.69	p
	o-PO ₄		0.36*	0.50*	-0.48*	r
			0.006	<0.0001	0.0002	p
	NH ₄		-0.18	0.49*	-0.16	r
			0.19	<0.0001	0.24	p
Lavaca- Colorado Estuary	SiO ₄		0.76*	0.14	-0.71*	r
			<0.0001	0.29	<0.0001	p
	o-PO ₄		0.80*	-0.07	-0.51*	r
			<0.0001	0.55	<0.0001	p
	NH ₄		0.28*	0.71*	-0.30*	r
			0.01	<0.0001	0.005	p
Lavaca- Colorado Estuary	o-PO ₄		0.07	0.48*	0.067	r
			0.49	<0.0001	0.54	p
	NH ₄		0.05	0.20	-0.61*	r
			0.67	0.06	<0.0001	p
	NO ₂₊₃		-0.05	0.16	-0.06	r
			0.66	0.15	0.53	p

* denotes significant value

2.4. Discussion

2.4.1. Existing Inorganic Nutrients and Total Suspended Solids

In the past, inorganic nutrient limitations in the estuaries were compared with half saturation constant (HSC) nutrient concentration as the standard concentration. The half saturation constant nutrient concentration is known as the amount at which nutrient uptake is half of the maximum value (Fisher et al. 1988). Below half saturation constant the uptake rate is reduced limiting algal growth (Fisher et al. 1988). The half saturation constant for nitrate, nitrite and ammonia to grow coastal phytoplankton is 1-2 $\mu\text{mol/L}$ each, whereas for o-PO_4 it is 0.1-0.5 $\mu\text{mol/L}$ (Fisher et al. 1988; Sanders et al. 2001). Only 13 NO_{2+3} concentrations out of 56 observations in the Guadalupe, 6 out of 70 in the Nueces and 25 out of 84 in the Lavaca-Colorado Estuaries were equal to or greater than half saturation constant. Most importantly those equal to or greater than half saturation constant were from near stations. In contrast to NO_{2+3} concentrations, most of the o-PO_4 concentrations were equal to or greater than half saturation constant with the exceptions from Nueces and Lavaca-Colorado Estuaries' far stations. In the Nueces Estuary, the average near and far stations NH_3 and NO_{2+3} concentrations were most of the time less than 1 $\mu\text{mol/L}$ (Fig. 2.2). These results indicate the Nueces Estuary was NH_3 and NO_{2+3} limited for coastal phytoplankton growth in all stations, whereas o-PO_4 limitation in far stations. The Guadalupe Estuary though gets more inflow than the other two estuaries, showed NO_{2+3} limitations in the far stations. The Lavaca-Colorado estuary was NO_{2+3} limited in summer seasons. Oxidized forms of inorganic nitrogen, especially nitrate, was found to be abundant in Texas Estuaries (Hou et al. 2012), in contrast during the present study NO_{2+3} concentrations were found to be limited in all the three estuaries using HSC as the standard concentration. Most of the time TSS was less than

50 $\mu\text{mol/L}$ and the three year sampling periods was during low flow event, which could be the reason for low NO_{2+3} .

The half saturation constant to grow coastal phytoplankton for silicate is 1-5 $\mu\text{mol/L}$ (Fisher et al. 1988). Based on that, silicate (SiO_4) concentration in all three estuaries was not limited for coastal phytoplankton growth (Fig. 2.3). The significant difference in SiO_4 concentration at near and far stations in the Nueces Estuary indicates freshwater inflow was supplying SiO_4 in the estuary (Table 2.1). Past researchers have found SiO_4 minerals are active in controlling dissolved silicate concentration (Rickert 2000; Rickert et al. 2001). All the three estuaries' SiO_4 concentration close to 100 $\mu\text{mol/l}$ in salinities greater than 20 ppt and TSS less than or equal to 50 mg/L may be due to the release of SiO_4 from diatom mineralization and resuspension. A laboratory experiment using the Guadalupe and Nueces Estuary sediments identified wind forcing can increase SiO_4 concentration in the water if the sediment contains silicate minerals (Paudel unpublished). Hence inflow, mineralization, and resuspension may be responsible for maintaining silicate concentration in these estuaries.

The present study findings relied on quarterly sampling to identify TSS-nutrient relationship in the Estuaries. The findings of long term sampling since 1987 and weekly sampling from Oct 2011 to Oct 2012 indicates there is low variability of nutrients and TSS in the Texas Estuaries, except in peak flow events. Generally, inorganic nitrogen and phosphorus were less than 0.5 $\mu\text{mol/L}$ in the long term and weekly samplings. Hence, we think quarterly sampling is sufficient to answer our research questions.

The long term average turbidity in Texas Coast showed high turbidity in secondary bays than primary bays of the Guadalupe and Lavaca-Colorado Estuaries (Montagna et al. 2013b), however, present study TSS was not significantly different between near and far stations in the Guadalupe Estuary (Table 2.1). TSS was significantly different between near and far stations in the Nueces and Lavaca-Colorado Estuaries. Rather the Guadalupe Estuary near and far stations TSS concentration were almost same. Wind and cold front events could have significant role to have high TSS concentration in the primary bay of the Nueces Estuary.

NH₃ was not significantly different between near and far stations in the three estuaries (Table 2.1). Silicate was only significantly different between near and far stations in Nueces Estuary. Orthophosphate was significantly different between near and far stations in Nueces and Lavaca-Colorado Estuaries but not in Guadalupe Estuary, while NO₂₊₃ was significantly different between near and far stations in Guadalupe Estuary (Table 2.1). These results indicate there may be a lack of sufficient river inflow to the estuaries to meet productivity needs.

2.4.2. Existing TSS – Inorganic nutrient relation

Nitrogen and phosphorus concentrations increased with the increase in estuary TSS concentration (Smith et al. 1996; Jickells et al. 2000). NO₂₊₃ identified to be increased from approximately 10 µmol/L to 25 µmol/L as TSS increased from 125 mg/L to 180 mg/L (Fig. 2.5). Though NH₃ increase was lower compared to NO₂₊₃ at the same range of TSS, overall dissolve inorganic nitrogen concentration increased at the fore mentioned TSS range. Relationship of NO₂₊₃ and NH₃ with TSS and chlorophyll-a indicates high TSS concentration is required to increase inorganic nitrogen concentration in the estuaries. TSS concentration of greater than 100 mg/L was identified during extreme events such as peak flow and frontal events. Generally, high

inflow accompanied by high TSS can transport dissolved NO_{2+3} from watershed to an estuary. Bottom organic debris, when recycled and resuspended, can release NH_4^+ (Morin and Morse 1999). Flux of NH_4^+ ion from the pore water oxidized in the water column to NO_3^- by nitrifying bacteria (Hartzell and Jordan 2012). High inflow and channel disturbance by wind can bring NH_4^+ ion in the water column, which gets oxidized in the shallow estuary resulted in the increase of NO_{2+3} concentrations. Ammonia desorbs from the sediment in the form of NH_4^+ as freshwater enters into the increased salinity gradient of estuaries (Giblin et al. 2010; Weston et al. 2010). Increase in NH_3 beyond 80 mg/L of TSS could be because of desorption of NH_3 from suspended sediment transported by high inflow. Furthermore, higher TSS concentration during frontal events thus may increase NO_{2+3} and NH_3 in the overlying water by desorption from suspended sediments and by enhancing mineralization. NO_{2+3} and NH_3 was not increasing below 125 mg/L of TSS concentration that could be because at lower TSS concentration the released NO_{2+3} and NH_3 get utilized by the biotic components in the system, and may not get detected.

The estuaries o-PO4 concentration ranged from below detection limit to 3 $\mu\text{mol/L}$ when compared with TSS and chlorophyll-a concentrations. Lower level of o-PO4 in the water column could be because of the adsorption of released P in the organic matter and calcite minerals (Paudel unpublished). Increase in o-PO4 concentration was identified to be related with chlorophyll-a and TSS concentration. At TSS of lower than 50 mg/L, o-PO4 was identified to be related with chlorophyll-a (Fig. 2.5). That indicates at lower turbidity remineralization was active and controlling o-PO4 concentration. o-PO4 concentration decreased as TSS increased from 100 to 150 mg/L that could be because of the adsorption of o-PO4 on clay particles or calcium carbonate shells (McGlathery et al. 1995; Staudinger et al. 1990; Froelich 1988; Spiteri et al. 2008). The gradual increase in o-PO4 concentration from near below detection limit to 2 $\mu\text{mol/L}$

as TSS increased from 150 mg/L might be due to the phosphate desorption and apatite dissolution $[Ca_5(PO_4)_3OH + H^+ \leftrightarrow 5(Ca^{2+}) + 3H_2PO_4 + H_2O]$ (Spagnoli and Bergamini 1997), though that dissolution is very slow.

Similar to o-PO₄, SiO₄ identified to be related with chlorophyll-a when TSS was lower than 50 mg/L. SiO₄ was greater than 100 µmol/L when TSS was greater than 150 mg/L (Fig. 2.5). In the Guadalupe Estuary during peak flow events the average SiO₄ concentration was more than 500 µmol/L (Montagna unpublished). Result of SiO₄ relationship with chlorophyll-a and TSS concentration indicates the presence of diatoms and silicate minerals in the estuaries might have been maintaining its concentration. Presence of silicate minerals in the sediments can maintain silicate concentration in the water column (Rickert et al. 2001). Low grade silica species and silicate minerals were identified in the Guadalupe, Lavaca-Colorado, and Nueces Estuaries sediments (Paudel unpublished). High inflow events accompanied by high TSS and churning of bottom sediment might be the reason for the high SiO₄ at high TSS concentration.

Nitrogen limitation relative to phosphorus is possible as the result of no human influence on excessive sediment load transport to the estuary (Paerl 2009; Nixon 1995; Howarth and Marino 2006). However, nitrogen limitation in all the three studied estuaries may not relate to any human influence on excessive load transport but may be due to the decrease in sediment loads supply to the estuaries. The decrease in sediment loads to the Nueces Estuary is due to the sedimentation in Lake Corpus Christi (Ockerman et al. 2013). As the sediment supply decreased, NH₄⁺ release by organic matter remineralization decreased, which then curtailed NH₄⁺ ion oxidation to NO₂ and NO₃. Low NH₃ concentration in the Nueces Estuary, where nitrogen limitation was the greatest, might be of low sediment supply. Low NH₃ and NO₂₊₃

concentrations obtained in the present study supports previous studies that showed nitrogen limitation in Texas Estuaries (Gardener et al. 2006; Hou et al. 2012).

PC1 in the Guadalupe Estuary and PC2 in the Lavaca-Colorado Estuary represent freshwater inflows, whereas PC2 in Lavaca-Colorado and PC1 in Guadalupe represent seasons. In the Guadalupe Estuary, TSS, NH_3 and NO_{2+3} concentrations relied on inflow, whereas in the Lavaca-Colorado Estuary NH_3 and NO_{2+3} concentration relied on inflow (Fig. 2.6a and 2.6b). In the Guadalupe Estuary, the PC2 axis showed that SiO_4 concentrations were somewhat related with seasonal changes. The change in season affects temperature and frontal events. Temperature affects nutrient recycling rates and front affects resuspension events, thus combination of both may have been responsible in SiO_4 concentration in the water. In the Lavaca-Colorado Estuary it showed that TSS and silicate concentrations were relied on seasonal changes. The resuspension of sediments due to the effects of frontal events may have affected TSS concentration. The estuaries sediments consist of significant amount quartz and silicate minerals (Paudel unpublished), which when resuspended might affect silicate concentrations.

In Nueces estuary, PC1 axis represents water clarity and showed that SiO_4 , o- PO_4 and chlorophyll depend on water clarity (Fig. 2.6c). TSS, salinity, and NH_3 had low variability. Low variability of these variables indicates low freshwater inflow in the Nueces Estuary. The less inflow events to the estuary may be the reason for the low nitrogen supply. The lack in supply of suspended loads from the watershed may have reduced inorganic nitrogen to the estuary. Chlorophyll-a, SiO_4 , and o- PO_4 were closely related that indicate water clarity accompanied by remineralization could increase SiO_4 and o- PO_4 concentration in the Nueces Estuary.

2.5. Conclusion

In South Texas precipitation has decreased for the past few years. Decrease in precipitation and increase in drought decreased inflow to the estuaries. This leads to the decrease in sediment load transport to the estuaries. The concentrations of nitrite+nitrate, ammonia, orthophosphate, and silicate of 15, 3, 1.5, and 100 $\mu\text{mol/L}$ were identified at high TSS concentration i.e. beyond 150 mg/L. The presence of low concentrations of inorganic nutrients and TSS could be because of less sediment loads transport to the estuaries. In most of the three estuaries water samples, dissolved nitrite+nitrate and ammonia were less than the half saturation constant, i.e. 1-2 $\mu\text{mol/l}$. The Nueces Estuary was found to be the most dissolved inorganic nitrogen limited, which was identified based on the half saturation constant for the nutrient. The findings of the study revealed that dissolved silicate, orthophosphate and ammonia concentration were correlated with TSS concentrations.

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CHAPTER III

MODELING INORGANIC NUTRIENT DISTRIBUTIONS AMONG HYDROLOGIC GRADIENTS USING MULTIVARIATE APPROACHES

Abstract

River inflow can control the distribution of dissolved inorganic nutrients in an estuary. So, it is expected that estuaries with different inflow will have different nutrient transport and different structural and functional balance of nutrient dynamics. A long term (1987-2012) data set of nutrients in the three South Texas Estuaries (the Guadalupe (GE), Lavaca-Colorado (LC), and Nueces (NC) Estuaries) was used to test these hypotheses. The nutrients in the estuaries were compared using multivariate linear regression and structural equation modeling (SEM). The estuaries are relatively oligotrophic because detecting ammonia, nitrite+nitrate, and orthophosphate concentrations each of $\leq 1 \mu\text{mol/L}$ in the Nueces Estuary had probabilities of 0.63, 0.75, and 0.64 respectively. Although the GE and LC Estuaries have more river inflow than the NC Estuary, the probability of detecting dissolved inorganic nitrogen (DIN) (ammonia+nitrite+nitrate) concentrations of $\leq 1 \mu\text{mol/L}$ was greater than 0.5. In all three estuaries, silicate was constantly available and was of high concentration throughout the 25 years, whereas inorganic nitrogen and phosphorus concentrations have decreased since 1987. The SEM identified that environmental-flow and phytoplankton were the most important predictor variables to predict DIN and other nutrients, whereas TSS was important in predicting phosphorous and silica. The direct negative effect of latent variable phytoplankton to DIN

implies remineralization is likely maintaining the supply of DIN concentrations. Environmental flow was identified as the most important predictor variable in maintaining DIN. However, the low path coefficient of environment flow to nitrogen and other nutrients indicate there is insufficient river inflow to maintain inorganic nitrogen and phosphorus concentration into the estuaries.

Keywords: Structural Equation Modeling; Multivariate linear regression; Inorganic nutrients; Environmental flow.

3.1. Introduction

Knowledge of spatial and temporal inorganic nutrient distribution helps in developing policies and applying sustainable management practices to maintain healthy estuary ecosystems. River inflow can control the distribution of inorganic nutrients in an estuary. Fluctuation of inorganic nutrients transported to the estuary affects the structural and functional balance of the ecosystem because the biotic community responds to sudden changes in inorganic nutrients. Seasonal dissolved nitrogen and dissolved orthophosphate loading affect the phytoplankton biomass in Chesapeake Bay (Malone et al. 1996). Other studies in the Chesapeake Bay have found that change in the floristic composition was due to the change in dissolved silicate concentration (Conley 1992; Adolf et al. 2006). Low inorganic nutrient concentrations in the Guadalupe, Nueces, and Lavaca-Colorado Estuaries during dry years was accompanied by low chlorophyll-a (chl-a) concentrations (Montagna and Palmer 2012).

Freshwater needs for water projects and diversions for irrigation have reduced the amount of freshwater input to estuaries. The conditions have become worse due to construction of dams, which not only curtail freshwater inflow but also reduce sediment and nutrient loading to an estuary (Montagna et al. 2002; Alber 2002; Jassby et al. 1995). In South Texas, the amount of inflow to the estuaries is also affected by the frequency of drought. A simulation study forecasting future precipitation has reported that in the 21st century South Texas will experience seasonal decreases in rainfall and increases in temperature (USGCRP 2009). The frequency of drought and need of freshwater inflow for the management of nutrient and sediment loadings to the estuary require identification and prediction of the variables that can control inorganic nutrients in the estuaries.

Varying freshwater inflow alters the inorganic nutrients concentrations in the Lavaca-Colorado, Nueces, and Guadalupe Estuaries (Montagna and Li 2010; Pollack et al. 2009; Palmer et al. 2011). However, a future management challenge lies in understanding direct, indirect, and interactive effects of environmental components for development of coastal management schemes (Cloern 2001). For instance the direct effect of inflow by altering flow volume and indirect effect of inflow resulted by altering water transparency might have a different magnitude of impact on the inorganic nutrient concentrations. Increase in flow volume has increased inorganic nutrients, likewise increase in fine suspended particles affects adsorption-desorption of inorganic nutrients. Identifying the roles of environmental components, thus, support in developing management policies.

The direct and indirect effects of different environment variables on the dynamics and pattern of biological components were identified by using structural equation modeling (SEM) (Malaeb et al. 2000; Grace and Pugasek 1997; Arhonditsis et al. 2007a, 2007b). Direct relationships between predictor and response variables were examined using multivariate linear regression (MLR) (Grace and Bollen 2005). In the present study SEM and MLR were used to identify direct and indirect effects of environment variables on the distribution of inorganic nutrients. Nutrient studies in estuaries have been biased towards temperate regions (Cloern 2001). Therefore the present study fills the gap by reporting on the long term dynamics of inorganic nutrients in the three South Texas Estuaries. Hence, the objectives of present study are: 1) to identify the long term (1987-2012) inorganic nutrient distribution in the Lavaca-Colorado, Guadalupe, and Nueces Estuaries using long term data, 2) to predict the inorganic nutrient concentration in the three estuaries by the application of structural equation modeling and multivariate regression, and 3) to identify the impact of different parameters on the change in the inorganic nutrient concentrations.

3.2. Materials and Methods

3.2.1. Study Area

The three South Texas Estuaries (Lavaca-Colorado, Guadalupe and Nueces Estuaries) are located in the Coastal Bend and have similar geomorphic structure and physiography (Fig. 3.1), but different hydrologic regimes (Table 3.1). The three estuaries consist of primary and secondary bays and are separated by a barrier island from the Gulf of Mexico. Inflow and precipitation decrease south of the Lavaca-Colorado Estuary with the Nueces Estuary getting the least amount of inflow. Due to the distinct climatic differences and lack of connection between watersheds each estuary is fed by different rivers. The Lavaca and Colorado Rivers drain into the Lavaca-Colorado Estuary. The San Antonio and Guadalupe Rivers confluence, and drains into the Guadalupe Estuary. The Nueces River drains into the Nueces Estuary. All three rivers have dams.

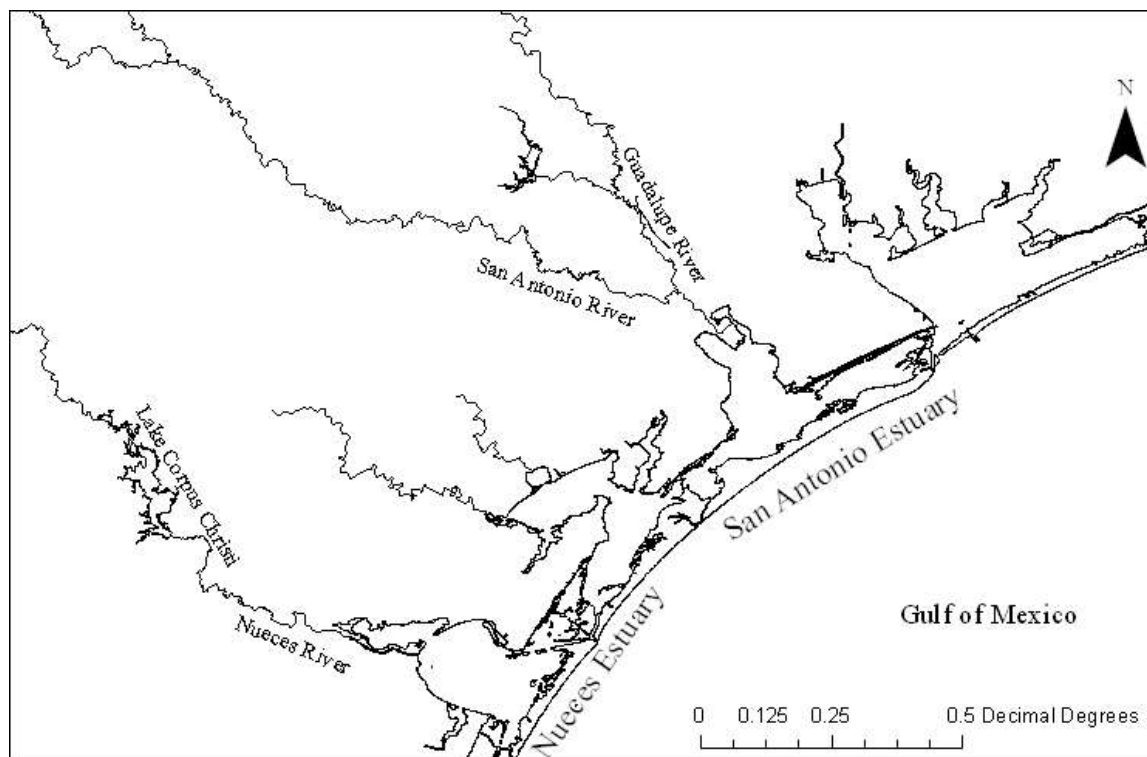


Fig. 3.1 Location of the three South Texas Estuaries.

Table 3.1 Location and climatic gradients of the three South Texas Estuaries.

Estuary	Latitude	Longitude	Area (km ²)	Rainfall (cm yr ⁻¹)	Salinity (ppt)	Inflow (10 ⁶ m ³ yr ⁻¹)
Guadalupe	28°24.4' N	96°42.7' W	551	91	16	2,677
Lavaca-Colorado	28°38.4' N	96°36.6' W	1,158	102	18	3,679
Nueces	27°51.6' N	97°29.0' W	433	76	23	346

Source: Latitude and Longitude from Russell and Montagna (2007); Area, Rainfall, salinity and Inflow from Montagna et al (2013)

3.2.2. Data description

Quarterly sampling (four per year) was performed to collect water quality data. The water quality variables used for the present study were temperature (temp), pH, dissolved oxygen (DO), salinity (sal), secchi depth, total suspended solids (TSS), volatile particulate organic matter (VOM), chlorophyll-a (chl-a), ammonia (NH_3) concentration, nitrite+nitrate (NO_{2+3}) concentration, orthophosphate (o-PO_4) concentration and silicate (SiO_4) concentration. Details on sample collection, sampling stations, water quality parameters, and procedures to measure water quality parameters are in several papers (Montagna and Kalke 1992; Pollack et al. 2009; Palmer et al. 2011; Kim and Montagna 2012). For inorganic nutrients analysis the best applicable range of method detection limit (MDL) recommended by the manufacturer of OIA Segmented Flow Auto analyzer are 0.1-10 $\mu\text{mol/L}$ for NH_3 , 0.02-10 $\mu\text{mol/L}$ for o-PO_4 , 0.35-35 $\mu\text{mol/L}$ for SiO_4 , and 0.02-40 $\mu\text{mol/L}$ for NO_{2+3} . The concentrations higher than detection limit were determined by sample dilution. During the data analysis concentrations lower than MDL were considered as 0 $\mu\text{mol/L}$.

The long term (1987-2012) nutrient analysis in the three estuaries were performed using long term data sets, whereas MLR and SEM were performed using short term data set (2010-2012). The short term data set contains all the parameters needed for our MLR and SEM development.

The three estuaries water quality parameters were log transformed in order to obtain normal distribution of residuals. Multivariate linear regression (MLR) was performed using individual estuary data sets, while structural equation modeling (SEM) was performed using the combined data set of the three estuaries. SEM did not have a good fit when using individual estuary data set; this could be because of small sample sizes, so the three estuary data sets were combined to

perform SEM. Before analyzing data using SEM seven missing values for NO₂₊₃ concentrations were replaced by the average value.

3.2.3. Model and Statistical Analysis

3.2.3.1. Structural Equation Modeling

Prediction of inorganic nutrients in an estuary requires exploratory and confirmatory analysis with the incorporation of direct and indirect effects of predictor variables on response variables. Structural equation modeling (SEM) is a multivariate statistical technique that uses factor analysis, regression analysis, and path analysis to evaluate the relationship between observed and latent variables (i.e., variables not directly measured) (Malaeb et al. 2000; Bentler 1992; Fan and Fan 2005). Structural equation modeling, unlike multivariate regression that includes directly measured variables, has the ability to represent variables that are not directly measured and can test indirect effects between explanatory variables (Reckhow et al. 2005).

In SEM, researchers use existing or empirical knowledge to build the model. One must specify a full model “a priori” and test that based on the observed variables. SEM is used to identify direct and indirect relationships between variables through analysis of covariance. In SEM, the model covariance matrix is tested with the observed data covariance matrix, thus the null hypothesis (H₀) that postulates the basic concept of SEM is—

$$H_0: \Sigma = \Sigma(\theta)$$

Where,

Σ = model calculated covariance matrix

$\Sigma(\theta)$ = observed data covariance matrix

SEM seeks acceptance of null hypothesis that is different to other hypothesis testing of linear model looking for the rejection of null hypothesis.

Some of the basic terminologies used in SEM are: exogenous variable, a variable not influenced by other variables; endogenous variable, a variable influenced by other variables; latent variable, a variable not measured directly; and manifest or observed or indicator variable, which is a directly measured variable. The structure model in SEM is used to relate all the variables needed to build a model, whereas the manifest model is used to relate indicator variables with latent variables and account the error variances in the model.

In the present study environment flow, water clarity, phytoplankton, nitrogen and dissolved components were the five latent variables. The indicator variables were temperature, salinity, total suspended solids (TSS), chl-a, secchi, silicate (SiO_4), orthophosphate (PO_4), ammonia (NH_3) and nitrite+nitrate (NO_{2+3}). Among those indicator variables, temperature and salinity were exogenous indicator variables, whereas SiO_4 , PO_4 , NH_3 , NO_{2+3} , TSS, chl_a, and secchi were endogenous indicator variables. The direct and indirect effects of exogenous and endogenous variables responsible in fluctuating inorganic nutrient concentration in the South Texas Estuaries were estimated by using SEM. SEM was used to predict inorganic nutrient distribution in relation to the change of different predictor variables. In the present study a standardized path coefficient was used to determine the relationship between latent variables. The standardized path coefficient explains the relationship between variables in terms of standard deviation (Grace and Bollen 2005). The identified path coefficient, thus, was the standard deviation obtained by one unit variation in predictor variable.

Knowledge acquired from the long term water quality monitoring in the South Texas estuaries was used as a foundation for building the structural and manifest model. In SEM, a structural model is formulated that depicts the relationship between latent variables environment flow, water turbidity, phytoplankton, nitrogen, and other dissolved inorganic nutrients. The manifest model was formulated to depict the relationship of measured variables salinity and temperature with environment flow, likewise chlorophyll-a with phytoplankton, NH_3 and NO_{2+3} with nitrogen, SiO_4 and o-PO_4 with other dissolved nutrients, and Secchi-depth and TSS with water turbidity.

3.2.3.1.1. Structural Equation Modeling Fit Evaluation

Sample size, estimation method, normality violation, and model specification are the potential contributing factors that may affect SEM model fit (Hu and Bentler 1998). In the present study maximum likelihood (ML) and generalized least squares (GLS) were used as the fitting function or estimation method to evaluate goodness of fit between observed and predicted covariance. Evaluation of model fit was performed using a chi-square test and descriptive measures (Schermelleh-Engel et al. 2003). The criteria for descriptive measure of fit evaluation were performed by the measures of overall model fit and by the measures of model comparison. Root mean squared error of approximation (RMSEA) was used as an index for overall model fit, while adjusted goodness of fit index (AGFI), goodness of fit index (GFI), Bentler's comparative fit index (CFI), Bentler and Bonnett's nonnormed fit index (NNFI), normed fit index (NFI), nonnormed index delta2 (DELTA2), McDonald's centrality index (CENTRALI), Bollen's normed fit index Rho1 (RHO1) were used as an index for model comparison (Schermelleh-Engel et al. 2003). Furthermore, the chi-square fit index and most of the descriptive fit indexes, except

RMSEA, NNFI, and CFI, are strongly biased towards sample size. RMSEA, NNFI, and CFI are rather biased toward model misspecification. Increasing number of sample size increases chi-square resulting in rejection of null hypothesis. Chi-square, thus, was also used as a descriptive measure of good fit by taking the ratio of chi-square and degree of freedom (Jöreskog and Sörbom 1993; Schermelleh-Engel et al. 2003). The goodness fit of observed and predicted covariance matrix was also tested by residuals, which is the difference between observed and predicted covariances. And the model fit was determined by the minimum difference between observed and model-predicted covariances.

3.2.3.2. Multivariate Linear Regression Model

Prediction of inorganic nutrient distribution in the estuaries and direct effects of each predictor variables on the response variables were performed by using multivariate linear regression (MLR). The significant model R-square, obtained while performing stepwise selection of predictor variable, was used as a criterion to select the linear model.

3.2.3.3. Probability distribution

The long term (1987-2012) inorganic nutrient concentrations of the three estuaries were divided into set of bins (intervals) and frequency distribution was calculated as the value occurred in that allocated bins. Set of bins were from 0 to 17 $\mu\text{mol/L}$ at the interval of 0.5 for o-PO₄ for all three estuaries. The set of bins were 0 to 25 $\mu\text{mol/L}$ for NH₃ and NO₂₊₃ for all the three estuaries at the interval of 0.5. For silicate set of bins were from 0 to 1300 $\mu\text{mol/L}$ for the GE estuary and 0 to 450 $\mu\text{mol/L}$ for the LC and NC Estuaries. The bin interval was at 5 $\mu\text{mol/L}$.

Probability distribution of nutrient concentration was then calculated using the frequency distribution of each concentration out of total number of samplings.

3.2.3.4. Analytical Software

In the present study SAS version 9.3 was used for the analysis. PROC CALIS was used for structural equation modeling. PROC REG stepwise selection method was used for multivariate linear regression analysis. PROC SGSCATTER was used to depict inorganic nutrient concentrations over 25 year period.

3.3. Results

3.3.1. Distribution of inorganic nutrients

Orthophosphate (o-PO_4) concentration in the three South Texas Estuaries has been decreasing since 1987; the date of sampling started (Fig. 3.2a). Probability distribution curve of o-PO_4 concentration showed that the probability of detecting concentration equal to or greater than $8\mu\text{m/L}$ in the Guadalupe (GE), $8\mu\text{m/L}$ in Lavaca-Colorado (LC), and $5\mu\text{m/L}$ in the Nueces Estuary was less than 0.01. The probability of detecting o-PO_4 concentration less than $0.5\mu\text{m/L}$ was 0.16, 0.34 and 0.38 in the GE, LC, and NC Estuaries respectively (Fig. 3.3a).

The long term (1987 to 2012) silicate (SiO_4) concentration was almost constant in the three estuaries, with the GE Estuary having higher concentrations compared to the LC and NC Estuaries (Fig. 3.2b). The probability of detecting silicate (SiO_4) concentration greater than or equal to $400\mu\text{m/L}$ in GE, $250\mu\text{m/L}$ in LC, and $300\mu\text{m/L}$ in NC was less than 0.01. The detection probability of SiO_4 concentration less than or equal to $5\mu\text{m/L}$ was 0.02, 0.07, and 0.06 in the GE, LC and NC Estuaries respectively (Fig. 3.2b).

Ammonia (NH_3) concentration in the Nueces Estuary has been decreasing since 1987, but in the LC and GE Estuaries NH_3 did not fluctuate very much (Fig. 3.2c). The probabilities of detecting NH_3 greater than or equal to $10\mu\text{m/L}$ in the GE, LC, and NC Estuaries were 0.03, 0.05, and 0.03 respectively. Furthermore, the probabilities of detecting NH_3 less than or equal to $1\mu\text{m/L}$ in the GE, LC, and NC Estuaries were 0.53, 0.50, and 0.63 respectively (Fig. 3.3c).

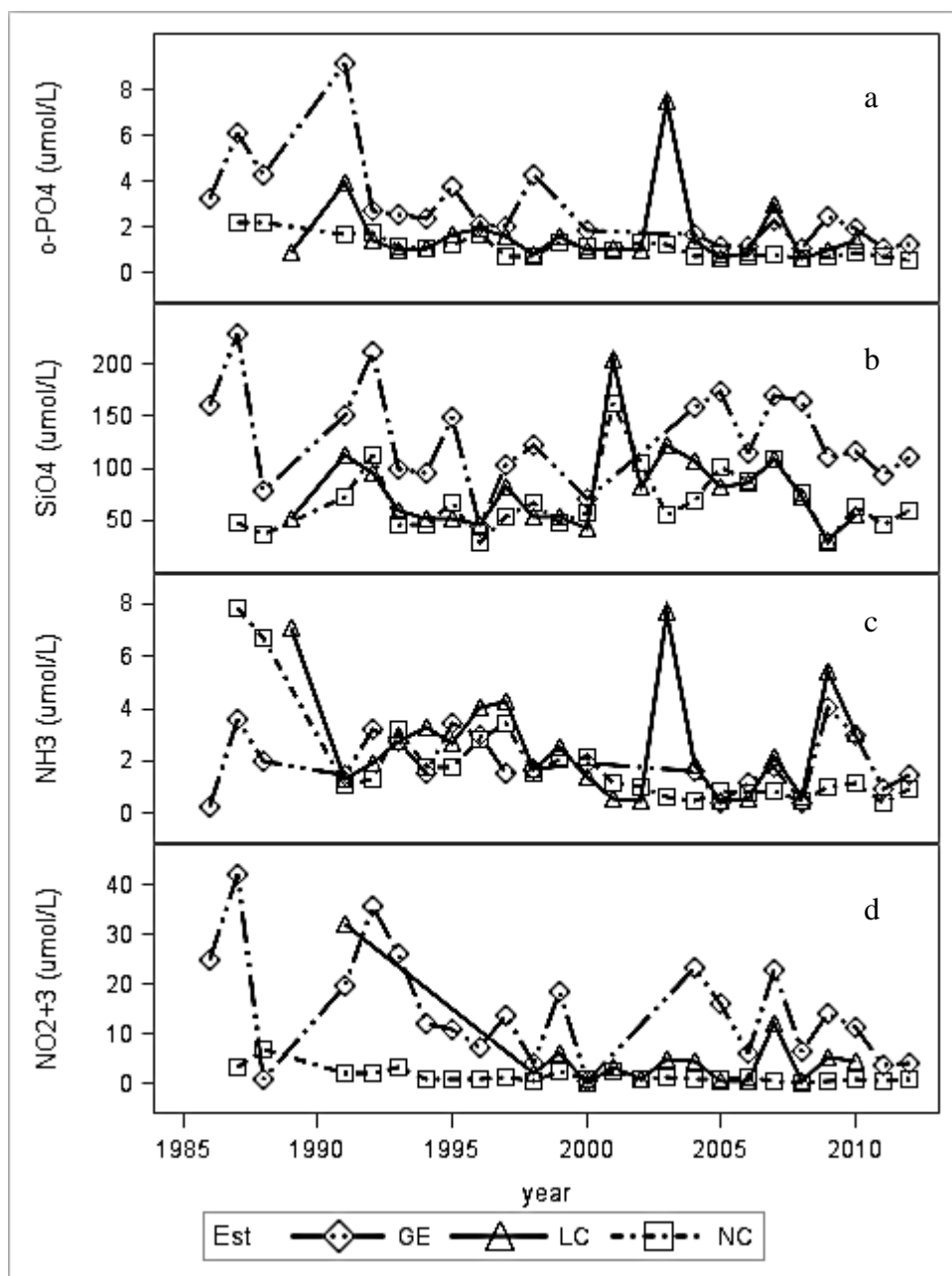


Fig. 3.2 Average inorganic nutrients in the Guadalupe (GE), Lavaca-Colorado (LC), and Nueces (NC) Estuaries from 1987 to 2012.

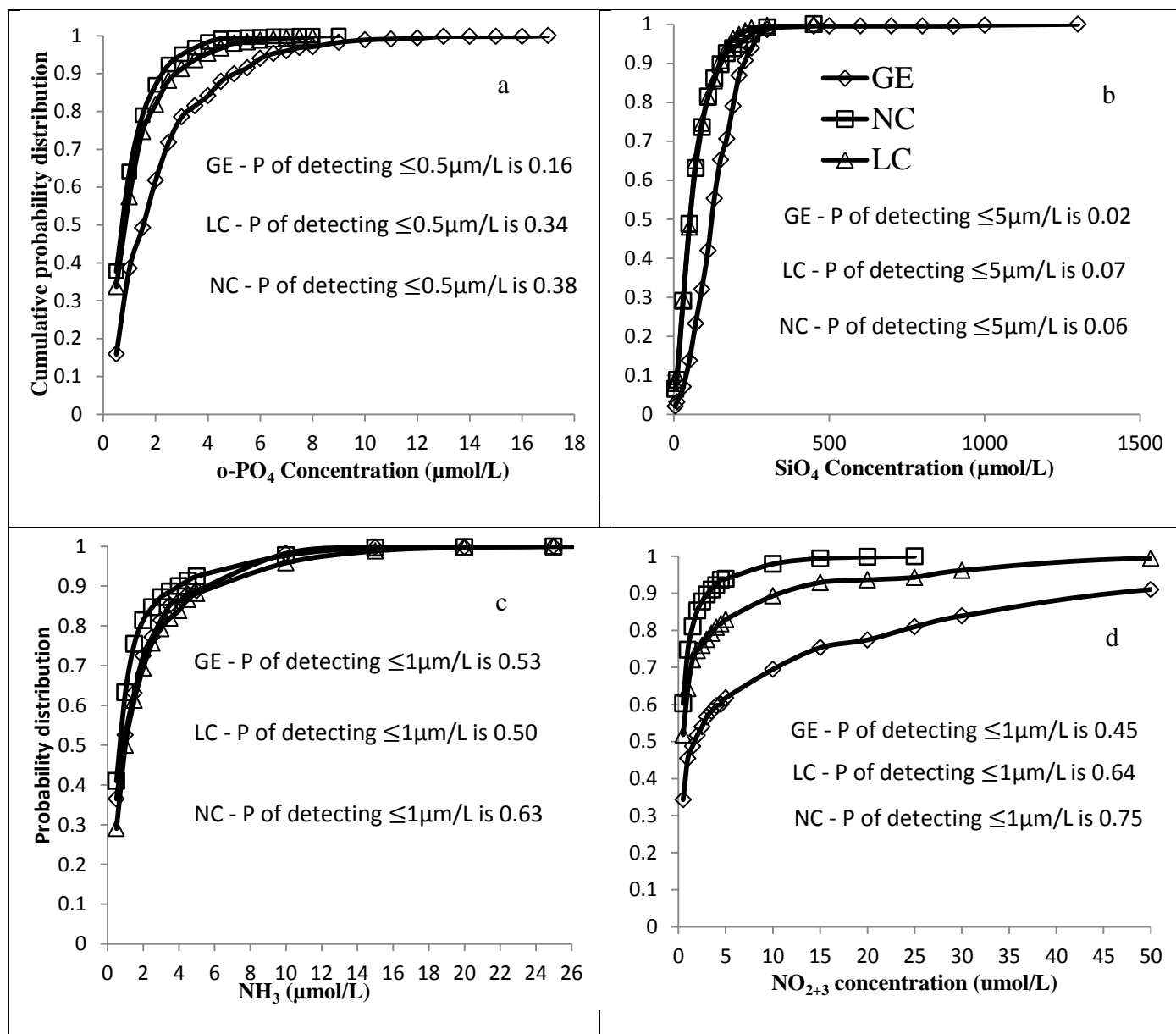


Fig. 3.3 Cumulative probability distribution of inorganic nutrients in the Guadalupe (GE), Lavaca-Colorado (LC), and Nueces Estuaries (NC) using long term (1987-2013) data. (a) o-PO₄ concentration in GE, LC and NC (b) SiO₄ concentration in GE, LC and NC (c) NH₃ concentration in GE, LC and NC (d) NO₂₊₃ concentration in GE, LC and NC. 'P' indicates probability.

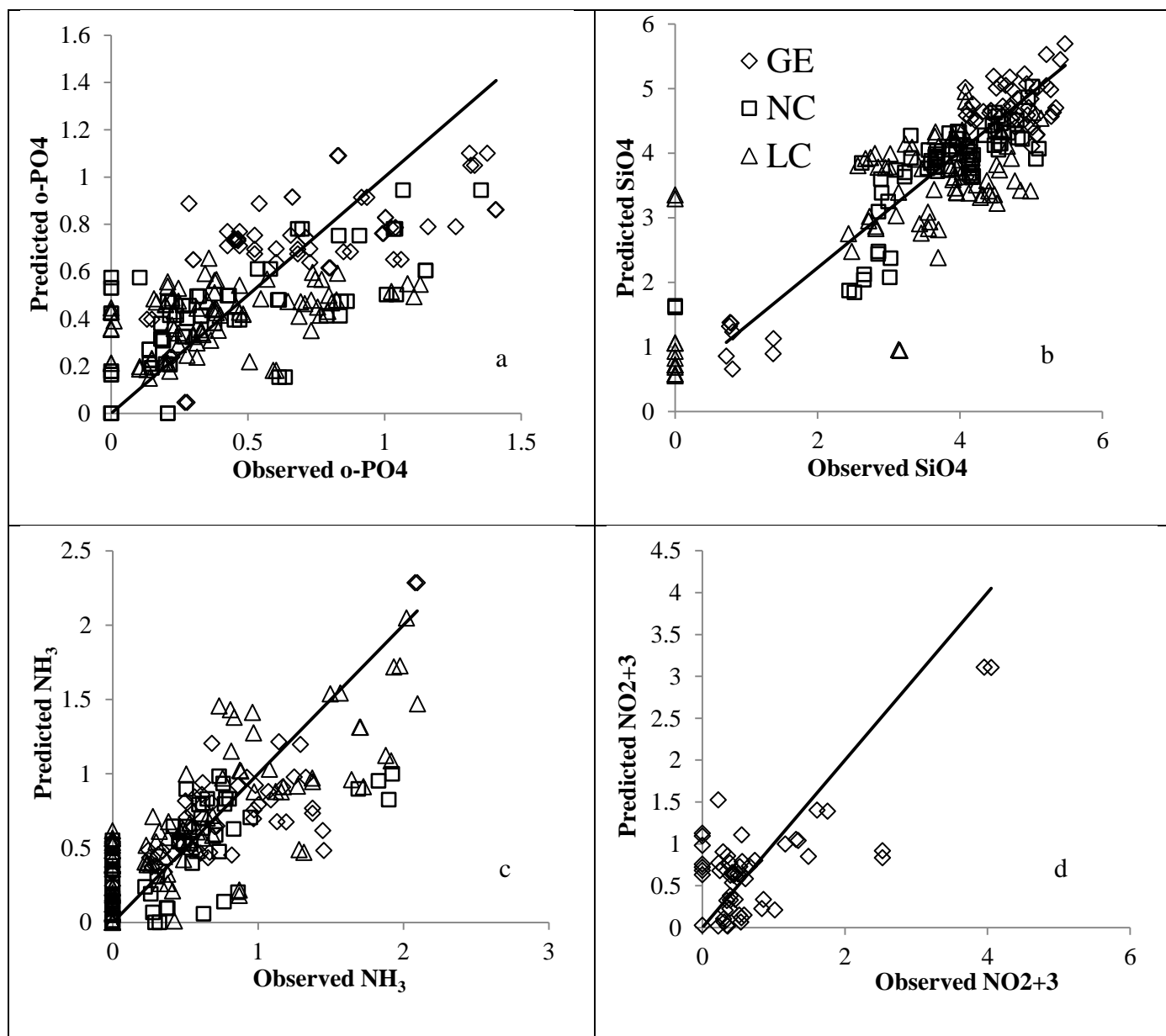


Fig. 3.4 Observed Vs Predicted inorganic nutrients in the Guadalupe (GE), Lavaca-Colorado (LC), and Nueces Estuaries (NC). All the values were log transformed. (a) Observed-predicted o-PO₄ in GE, LC and NC (b) Observed-predicted SiO₄ in GE, LC and NC (c) Observed-predicted NH₃ in GE, LC and NC (d) Observed-predicted NO₂₊₃ concentration in GE.

In the NC Estuary throughout the 25 years, nitrite+nitrate (NO_{2+3}) concentration was of very low concentration. In the three estuaries NO_{2+3} concentration has been decreasing since 1987. Even though the GE Estuary NO_{2+3} concentration was higher than the LC and NC Estuaries, NO_{2+3} in the GE Estuary was also decreasing since 1987 (Fig. 3.2d). The probabilities of detecting nitrite+nitrate (NO_{2+3}) greater than or equal to 15 $\mu\text{m/L}$ in the GE, LC, and NC Estuaries were less than 0.15, 0.07 and 0.01 respectively. The probability of detecting NO_{2+3} less than or equal to 1 $\mu\text{m/L}$ was 0.45, 0.64, and 0.75 in the GE, LC, and NC Estuaries (Fig. 3.3d).

3.3.2. Prediction of inorganic nutrient using multivariate linear regression

Dissolved oxygen (DO), pH, and temperature (temp) were the predictor variables to predict o- PO_4 in the GE (GE PO_4) and NC (NC PO_4) Estuaries (equations 3.1 and 3.3). MLR model r-square to predict o- PO_4 in the GE and NC Estuaries were 0.32 and 0.49 respectively. Most of the lower values were from the NC Estuary (Fig. 3.4a). Chlorophyll_a (chl), pH and salinity (sal) were the predictor variables to predict PO_4 in the LC Estuary (equation 3.2). Despite linear regression model R-square with the LC Estuary data was 0.19, points were shown in the graph. Equations (3.1), (3.2) and (3.3) were used to predict o- PO_4 concentrations in the GE, LC, and NC estuaries respectively.

$$\text{GEPO}_4 = 6.1375 + 1.8328 (\text{temp}) + 2.3970 (\text{DO}) - 7.4494 (\text{pH}) \quad (3.1)$$

$$\text{LCPO}_4 = -11.4765 + 0.1585 (\text{chl}) + 0.3901 (\text{sal}) + 4.6170 (\text{pH}) \quad (3.2)$$

$$\text{NCPO}_4 = 28.1433 + 1.4332 (\text{temp}) + 1.9759 (\text{DO}) - 16.4725 (\text{pH}) \quad (3.3)$$

Chlorophyll_a, total suspended solid (TSS), volatile particulate organic matter (VOM), temperature, salinity, and pH were the predictor variables to predict SiO₄ concentration in the GE (GESiO₄) estuary (equation 3.4), whereas chlorophyll_a, temperature, and pH were the predictor variables to predict SiO₄ concentration in the LC (LCSiO₄) and NC (NCPO₄) Estuaries (equations 3.5 and 3.6). MLR model r-square to predict SiO₄ in the GE, LC and NC Estuaries were 0.85, 0.57 and 0.69 respectively. Equations (3.4), (3.5), (3.6) were used to predict SiO₄ concentration in the GE, LC, and NC Estuaries. Most of the predicted values were close with the observed value, except few outliers from the NC and LC estuaries.

$$\text{GESiO}_4 = 60.126 - 0.6301 (TSS) + 0.6687 (chl) + 4.2854 (temp) - 0.8847 (sal) - 30.7171 (pH) + 0.7408 (VOM) \quad (3.4)$$

$$\text{LCSiO}_4 = 64.9956 + 0.6238 (chl) + 3.3902 (temp) - 33.3176 (pH) \quad (3.5)$$

$$\text{NCSiO}_4 = 32.4226 + 0.6250 (chl) + 2.2229 (temp) - 16.7841 (pH) \quad (3.6)$$

Salinity and TSS were the predictor variables to predict NH₃ in the GE Estuary (equation 3.7), whereas salinity, temperature, and DO were the predictor variables in the LC Estuary (equation 3.8). In the NC Estuary, chlorophyll_a, salinity, and pH were the predictor variables to predict NH₃ (equation 3.9). MLR model r-square to predict NH₃ in the GE, LC and NC Estuaries were 0.65, 0.63 and 0.48 respectively. There were significant outliers from all three estuaries, mostly related with the observed value identified as 0 µm/L. Equations (3.7), (3.8), and (3.9) were used to predict NH₃ concentration in the GE, LC, and NC Estuaries respectively.

$$\text{GENH}_3 = 2.1361 + 0.1487 (TSS) - 0.6422 (sal) \quad (3.7)$$

$$LCNH_3 = 20.0638 - 1.0546 (temp) - 3.0897 (sal) - 2.5089 (DO) \quad (3.8)$$

$$NCNH_3 = 36.7923 + 0.3055 (chl) - 2.0895 (sal) - 13.2867 (pH) \quad (3.9)$$

In the GE Estuary, volatile particulate organic matter (VOM), dissolved oxygen, chlorophyll_a and salinity were the predictor variables to predict NO_{2+3} concentration (equation 3.10) with r-square of 0.43, whereas the linear regression model R-square was not significant for the prediction of NO_{2+3} with the LC and NC Estuaries data. Equation (3.10) was used to predict NO_{2+3} concentration in the GE Estuary.

$$GENO_{2+3} = -2.6337 + 1.2590 (VOM) + 0.2183 (DO) - 0.4532 (chl) - 0.0357 (sal) \quad (3.10)$$

3.3.3. Structural Equation Modeling

3.3.3.1. Model selection and suitability

The initial model was developed with direct path from environment flow to water turbidity, phytoplankton, nitrogen, and other dissolved nutrients. The indirect path from the initial model was from environment flow to turbidity and from turbidity to nitrogen and other dissolved nutrients. Likewise another indirect path was from environment flow to phytoplankton and from phytoplankton to nitrogen and other dissolve nutrients (Fig 3.5). The evaluation of fit indices of the hypothesized initial model were GFI= 0.9781, AGFI= 0.8027, RMSEA= 0.1312, probability of close fit= 0.0021, Hoelter critical N= 106, parsimonious GFI= 0.1358, and $\chi^2/df = 5.63 (= 28.16/5)$. The process for model selection requires running different alternative models. The fit indices of the alternative model that had the closest fit using ML estimation method were GFI=0.9895, AGFI=0.9059, RMSEA=0.0784, probability of close fit=0.1492, Hoelter critical N

=225, parsimonious GFI=0.1374, and $\chi^2/\text{df} = 2.65$ ($= 13.26/5$). This result indicated the alternative model has a better fit than the initial model. In the alternative model a direct path from TSS to nitrogen and other dissolved nutrients was included. In addition, the direct paths from environment flow to phytoplankton, from water turbidity to nitrogen, and from water turbidity to other dissolved nutrients were removed (Fig 3.6). On the basis of the fit indices, the alternative model was accepted. The alternative model was able to explain 54% variation in nitrogen and 38% variation in other dissolved nutrients. The model fit indices obtained by using MLS and GLS estimation methods were similar (Table 3.2).

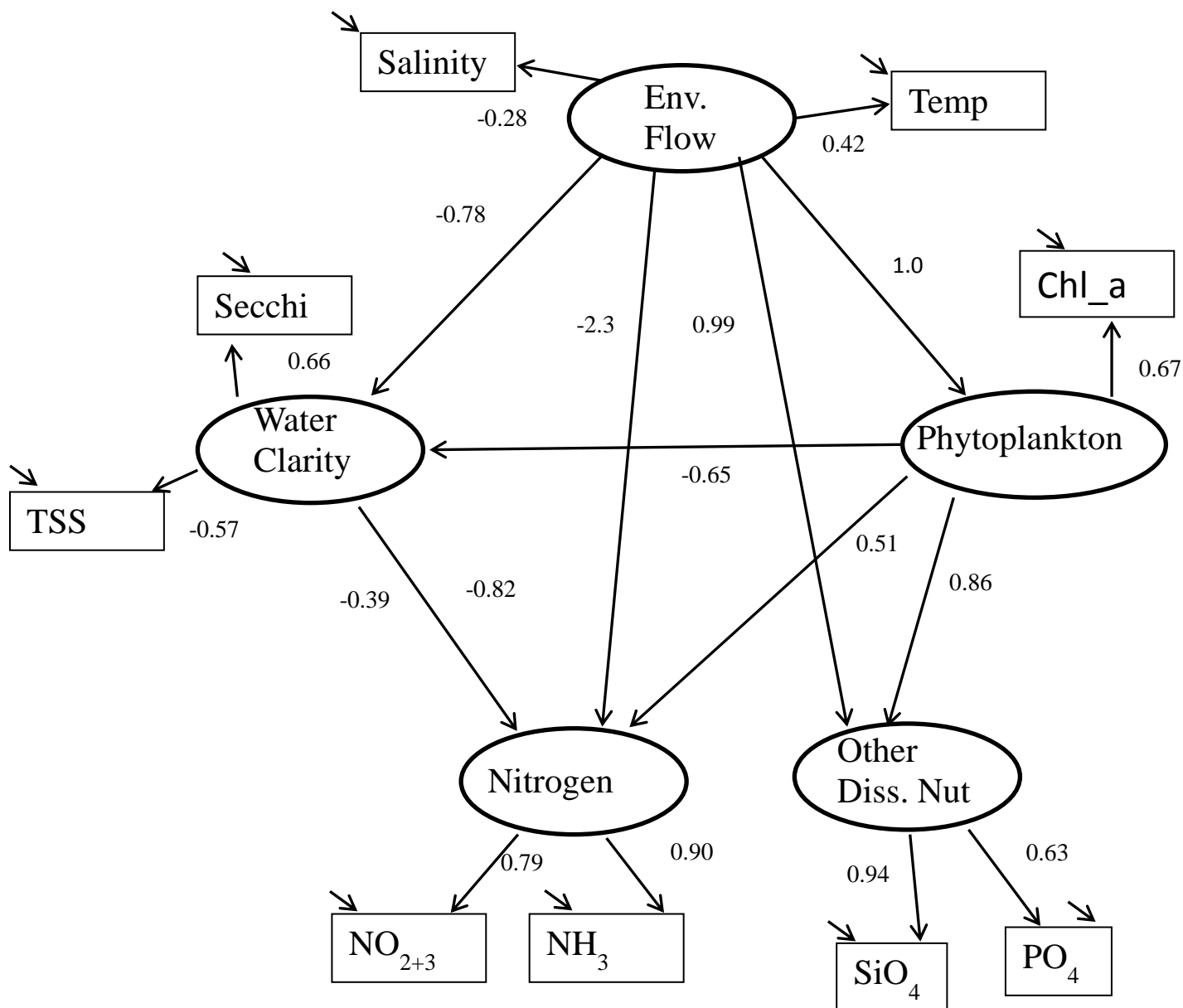


Fig. 3.5 Initial general model to predict nitrogen and other dissolved nutrient in the South Texas Estuaries. Variables in the ovals are latent variables, while variables in the rectangular boxes are measured or indicator variables. Small arrows in the measured variables indicate error. Abbreviation: Env Flow= Environmental flow, Temp= Temperature, Chl_a= Chlorophyll_a, Secchi= Secchi depth, Other Diss. Nut= Other dissolved nutrients

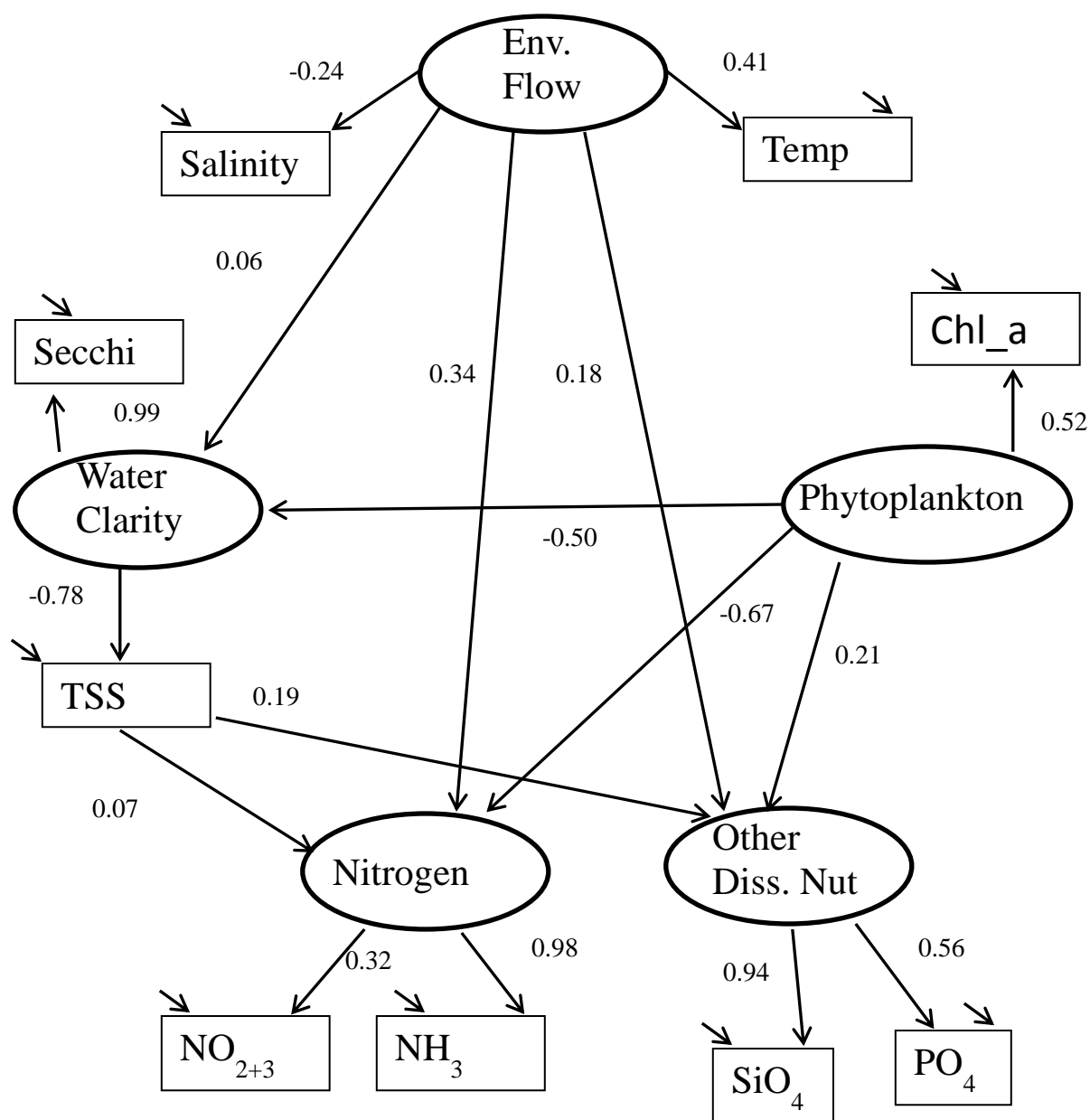


Fig. 3.6 Alternative specific model with path coefficients. Abbreviation: Env Flow= Environmental flow, Temp= Temperature, Chl_a= Chlorophyll_-a, Secchi= Secchi depth, Other Diss. Nut= Other dissolved inorganic nutrients (DNs)

Table 3.2 Model fit indices obtained for Maximum likelihood and generalized least square estimation method. Abbreviation: H Critical N= Hoelter Critical N, RMSR= root mean square residual, GFI= goodness of fit index, AGFI= Adjusted goodness of fit index, PGFI= Parsimonious goodness of fit index, RMSEA= Root mean square estimate approximation, P = probability, B-B NFI= Bentler-Bonett normed fit index, Bentler CFI= Bentler's comparative fit index.

Model	Model Fit	Estimation method	
Evaluation	indices	Maximum	Generalized
Indexes		likelihood	least square
Absolute	$\frac{\chi^2}{df}$	$\frac{13.26}{5}$	$\frac{13.33}{5}$
Index			
	H Critical N	225	224
	RMSR	0.0110	0.0122
	GFI	0.9895	0.9890
Parsimony	AGFI	0.9059	0.9009
Index			
	PGFI	0.1374	0.1374
	RMSEA	0.0784	0.0787
	RMSEA lower	0.0279	0.0284
	RMSEA upper	0.1310	0.1313
	P of close fit	0.1492	0.1469
Incremental	Bentler CFI	0.9890	0.9666
Index			
	B-B NFI	0.9832	0.9533

3.3.3.2. Prediction using alternate model

The direct paths from TSS and environmental flow to nitrogen were weaker, i.e. 0.07 and 0.24 respectively, than the direct path from phytoplankton to nitrogen, but the path is negative, i.e. -0.57 (Fig 3.6). The three direct paths from TSS, environment flow and phytoplankton to other dissolved nutrient were almost similar (0.19, 0.16, 0.21 respectively), with slight stronger path from phytoplankton. Calculated t-values to test the significance of path coefficient did not exceed the critical value 2.59 (N=270) at 10% level of significance. The calculated t-values to test the path coefficient from environmental flow and TSS to nitrogen, and from phytoplankton to other dissolved nutrients were less than the critical value 1.96 at 5% level of significance (Table 3.3). The indirect paths from environmental flow to nitrogen, and other dissolved nutrients were obtained by the product of segment from environment flow to water turbidity and from TSS to nitrogen and other dissolved nutrients. The indirect path thus calculated from environmental flow to nitrogen was 0.01 ($0.27 \times 0.76 \times 0.07$), which was very weak than the direct path. Similarly, the indirect path from environmental flow to other dissolved nutrients was 0.04 ($0.27 \times 0.76 \times 0.19$), very weaker than the direct path (Fig 3.6). The model identified strong path from phytoplankton to water turbidity (0.31) compared to path from environmental flow to water turbidity (0.27).

Table 3.3 Standardized direct effects of predictor variables on predicted variables. Abbreviation: ODN= other dissolved nutrients.

	Env. Flow	Phytoplankton	TSS	
Nitrogen	0.34	-0.57	0.07	Path coefficient
	(0.13)	(0.22)	(0.08)	Standard error
	[1.81]	[2.59]	[0.82]	t-value
ODN	0.21	0.16	0.19	Path coefficient
	(0.09)	(0.097)	(0.08)	Standard error
	[2.33]	[1.63]	[2.37]	t-value

Table 3.4 Obtained correlated matrix using ML estimation method with model predicted values and residuals. Abbreviation TEMP=temperature, SAL=salinity, CHL=chlorophyll-a.

	logSiO ₄	logNH ₃	logNO ₂₊₃	logTEMP	logSAL	logTSS	logCHL	logSECCHI	logPO ₄	Variable type and residual
logSiO ₄	1.00									Observed
	1.00									Predicted
	0.00									Residual
logNH ₃	0.15	1.00								Observed
	0.17	0.98								Predicted
	0.02	0.02								Residual
logNO ₂₊₃	0.12	0.32	1.00							Observed
	0.15	0.30	0.99							Predicted
	-0.03	0.02	0.01							Residual
logTEMP	0.53	-0.04	-0.15	1.00						Observed
	0.56	-0.06	0.05	1.00						Predicted
	-0.03	0.02	0.20	0.00						Residual
logSAL	-0.23	-0.46	-0.42	-0.09	1.00					Observed
	-0.19	-0.42	-0.41	-0.18	0.97					Predicted
	-0.04	-0.04	-0.01	0.09	0.03					Residual
logTSS	0.41	0.19	0.05	0.38	-0.20	1.00				Observed
	0.36	0.06	0.05	0.37	-0.21	1.00				Predicted
	0.05	0.13	0.00	0.01	0.01	0.00				Residual
logCHL	0.56	0.11	0.11	0.49	-0.33	0.35	1.00			Observed
	0.57	0.09	0.08	0.51	-0.29	0.35	0.99			Predicted
	0.01	0.02	0.03	-0.02	-0.04	0.00	0.01			Residual
logSECCHI	0.40	-0.21	-0.04	-0.47	0.27	0.59	-0.48	1.00		Observed
	0.43	-0.08	-0.07	-0.44	0.25	0.59	-0.49	1.00		Predicted
	-0.03	-0.13	0.03	-0.03	0.02	0.00	-0.01	0.00		Residual
logPO ₄	0.56	0.08	0.15	0.16	-0.22	0.16	0.40	-0.27	1.00	Observed
	0.56	0.10	0.09	0.18	-0.11	0.22	0.38	-0.26	0.99	Predicted
	0.00	-0.02	0.06	-0.02	-0.11	-0.06	0.02	-0.01	0.01	Residual

The correlation matrix using the ML method showed observed and predicted values were closely related. The five highest residuals between observed-predicted $\log\text{NO}_{2+3}$ - $\log\text{TEMP}$, $\log\text{NH}_3$ - $\log\text{TSS}$, $\log\text{NH}_3$ - $\log\text{SECCHI}$, $\log\text{SAL}$ - $\log\text{PO}_4$, and $\log\text{TEMP}$ - $\log\text{SAL}$ were 0.20, 0.13, -0.13, -0.11, and 0.09 respectively (Table 3.4).

3.4. Discussion

3.4.1. Distribution of inorganic nutrients

For decades, increases in dissolved inorganic nutrient concentrations in Gulf of Mexico estuaries have been of great concern. Researchers have found increasing inorganic nitrogen and phosphate in the coastal waters of Gulf of Mexico (Nixon 1995; Conley 2000; Bricker et al. 2008; Rabalais et al. 2002a, 2000b). In contrast the present study identified a decrease in dissolved inorganic nitrogen (ammonia and nitrite+nitrate) and orthophosphate concentrations since 1987 in the three South Texas estuaries (Lavaca-Colorado, Guadalupe, and Nueces) (Fig 3.2). In all three estuaries, the probability of detecting dissolved inorganic nitrogen (ammonia and nitrite+nitrate) lower than the half saturation constant required to grow coastal phytoplankton (1-2 $\mu\text{m/L}$ each of ammonia, nitrate and nitrite stated by Fisher et al. (1988) was more than 0.5. In the Nueces Estuary alone, the probability of detecting less than 1 $\mu\text{m/L}$ of dissolved nitrogen was 0.69. Orthophosphate concentration was also the lowest in the Nueces Estuary compared to the Guadalupe and Lavaca-Colorado Estuaries. The long term average chlorophyll-a concentrations were 11.2, 8.17, and 5.3 $\mu\text{g/L}$ in the Guadalupe, Lavaca-Colorado, and Nueces Estuaries respectively. In the Nueces Estuary, compared to the other two estuaries, the presence of low inorganic nutrients could be the reason for the low long term (1987-2012) average phytoplankton biomass. In the three estuaries, the long term silicate concentration was always greater than the half saturation constant, i.e. 5 $\mu\text{m/L}$ stated by Fisher et al. (1988), required to grow coastal phytoplankton. Silicate in the Guadalupe and Nueces Estuaries was maintained by inflow and by sediment silicate minerals (Paudel unpublished). The long term chlorophyll-a concentration, an indicator of phytoplankton biomass, was regulated by dissolved

nitrogen and dissolved phosphate in the three South Texas Estuaries. Low DIN to orthophosphate ratios in the Nueces Estuary also indicates that phytoplankton biomass was controlled by those two nutrients.

The three estuaries lie in a gradient of decreasing rainfall and thus decreasing freshwater inflow. The Lavaca-Colorado estuary has more rainfall than the Nueces and Guadalupe Estuaries (Table 3.1). Annual average surface inflow data from Texas Development Water Development Board showed that the Lavaca-Colorado Estuary has more annual inflow than the Guadalupe and Nueces Estuaries (Fig 3.7). Though the Lavaca-Colorado Estuary has more inflow than the Guadalupe Estuary, the surface area of the former is almost double than the latter. Thus, the transported nutrient signals are more dilute in the Lavaca-Colorado Estuary than in the Guadalupe Estuary. This is the likely reason for the lower inorganic nutrient concentration in Lavaca-Colorado estuary compared to Guadalupe Estuary.

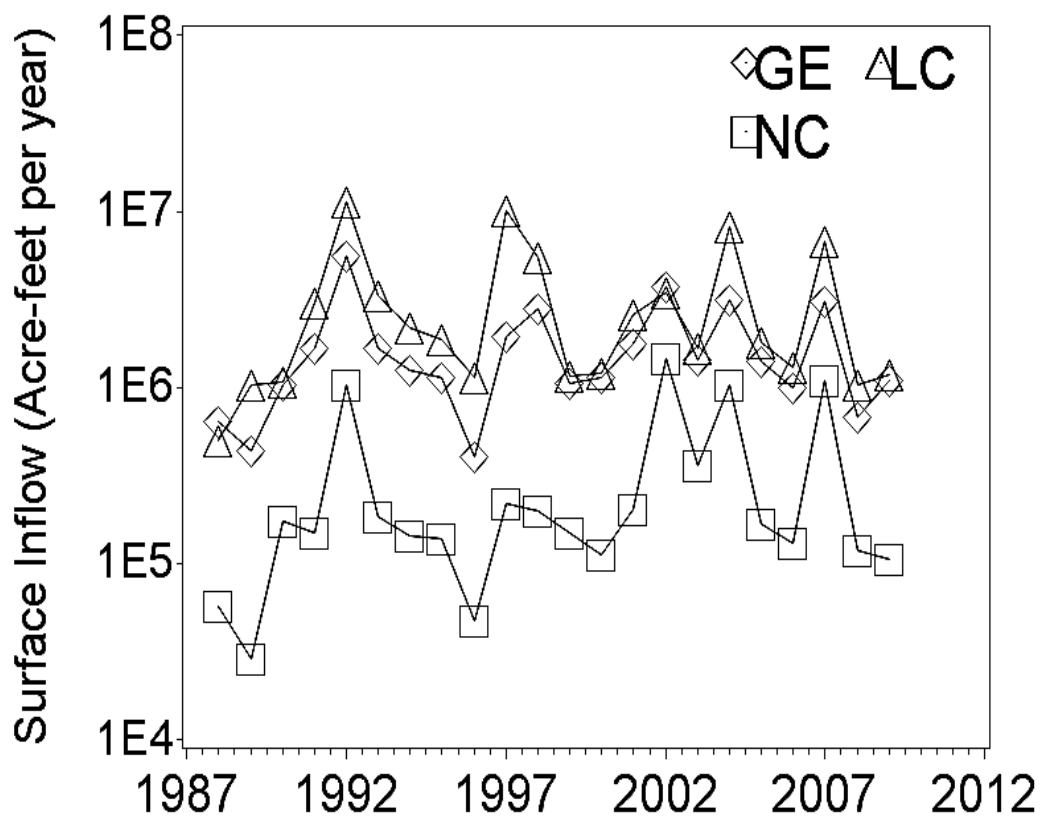


Fig. 3.7 Annual average surface inflow in the Guadalupe (GE), Lavaca-Colorado (LC), and Nueces (NC) Estuaries from 1989 to 2009. Data of annual average surface inflow was from Texas Water Development Board.

High inflow events in South Texas Estuaries are characterized by high levels of nutrient concentrations, and the Nueces Estuary did have more nutrients during high inflow events. However, the presences of channel diversions and Lake Corpus Christi dam, which collects most of the water for municipal and irrigation use, have affected the surface inflow to the Nueces Estuary (Montagna et al. 2009). The reduced rainfall and dam have decreased surface inflow to the Nueces Estuary by 10 orders of magnitude than the Lavaca-Colorado and Guadalupe Estuaries. Even during high inflow events, the Lavaca-Colorado Estuary and Guadalupe Estuary average surface flows were respectively 9 and 6 times higher than the Nueces Estuary surface flow (Fig 3.7). Past research has found that the nitrogen supply by inflow to the Nueces Estuary was half of the wastewater discharge (Brock 2001). However, the reduced surface inflow might have a significant effect for the low inorganic nitrogen and phosphorus concentrations in the Nueces Estuary, as compared to the other two estuaries.

3.4.2. Predicting inorganic nutrient

Among the multivariate data analyzing methods, structural equation modeling (SEM) is considered as the method that incorporates high theoretical contents whereas multivariate linear regression (MLR) is that of low theoretical contents (Grace 2006). Models based on high theoretical content are considered the most rigorous models in predicting and evaluating complex a-priori hypothesis. However, low theoretical content models like MLR are important for development of predictive equations (Grace 2006). Our multivariate data analyzed with both high and low theoretical content identified direct and indirect components that are important for the management of inorganic nutrients in estuaries. SEM identified both direct and indirect

effects for predictor variables maintaining nutrients. In contrast, only direct effects of measured predictor variables were identified by evaluating coefficients of MLR.

In the Guadalupe and Nueces Estuaries, pH was one of the variables to predict o-PO₄ concentration with a significant r^2 value (equation 3.1 and 3.3). In both estuaries it was predicted that increase in pH decreases o-PO₄ concentration, which might be possible by the presence of calcite in sediments. As pH increases, o-PO₄ released from the sediment water interface and transported to the epilimnion, where it can be adsorbed in the calcite (Staudinger et al. 1990). Another recent study in the Guadalupe and Nueces Estuaries has found calcite minerals in the sediments (Paudel unpublished). The increase in pH thus might be controlling o-PO₄ concentration in the estuaries because of the presence of calcite in the sediments. Increase in o-PO₄ concentration with the increase in temperature and DO indicate microbial mineralization of organic matter might be another important factor for the o-PO₄ concentration in the Guadalupe and Nueces Estuaries.

In all the three estuaries, chlorophyll-a, pH, and temperature were the common predictor variables to predict silicate concentrations. This indicates recycling and mineralization of sediment organic component might be maintaining silicate concentrations.

In the three estuaries, increase in salinity was responsible for the decrease in ammonia concentration. This implies freshwater inflow was important in transporting ammonia in the three estuaries. Similar to ammonia, in the Guadalupe estuary NO₂₊₃ concentration was negatively related with salinity, which also implies the importance of freshwater inflow in transporting NO₂₊₃.

3.4.3. Prediction and evaluation of complex a priori hypothesis

Based on model performance and model suitability using existing knowledge, SEM identified the condition of inorganic nutrient distribution patterns in the three South Texas Estuaries. An initial model was constructed and tested for model fit. Several alternative models were run and the fit indices using ML and GLS estimation method were checked to identify goodness of fit. The alternative model shown in Fig. 3.6 worked better than the initial model. The alternative model was also checked regularly with the new available data collected from the field. To compare MLR results with SEM results we included pH and DO in the SEM model, however we did not obtain good fit and t-value to determine the path coefficients were not significant, so pH and DO was dropped in our final SEM model.

In SEM, the standardized path coefficient expressed the relationship between variables in terms of standard deviation and can be easily compared to interpret relationships (Grace and Bollen 2005). The direct standardized path coefficient from environment flow to nitrogen indicates there would be 0.34 standard deviation increase in nitrogen concentration at every unit standard deviation increase in environmental flow, if the effects from phytoplankton and TSS remain constant. Likewise increases in phytoplankton by one unit standard deviation would decrease nitrogen concentration by -0.57 standard deviation, if the effects from TSS and environment flow remain constant. Environmental flow, phytoplankton, and TSS affected the dissolved nitrogen concentration in the estuaries, though TSS had very negligible effect. Environment flow was the significant factor in controlling the estuaries nitrogen concentration, while phytoplankton was responsible in utilizing nitrogen. Other studies have found a direct path from nitrogen to phytoplankton (Arhonditsis et al. 2007a, 2007b; Arhonditsis et al. 2006).

However in the present study, good fit was obtained with the inclusion of a path from phytoplankton to nitrogen, but not from nitrogen to phytoplankton. Recycling and mineralization of organic matter are the two important processes that balance nutrients in the South Texas Estuaries, and this is a possible reason for the high phytoplankton effects on nitrogen concentration.

Almost equal levels of direct effects were identified from environmental flow, phytoplankton, and TSS on other dissolved nutrients. Among them environmental flow has slightly higher standardized path coefficient than the other two. An increase in one unit standard deviation of phytoplankton would increase 0.16 standard deviation of other dissolved nutrients, which indicates mineralization in the estuaries could provide other dissolved nutrients. The positive effects of phytoplankton on other dissolved nutrients could be because of the lack of diatoms in the estuaries. Otherwise, diatoms could have pumped out silicate resulting in negative effects on other dissolved nutrients. Silicate concentration in the Guadalupe Estuary was high during peak inflow events, a few concentrations were greater than 1000 $\mu\text{m/L}$ at the station closest to the river mouth (Paudel et al unpublished). Even the Nueces Estuary, which gets less inflow than other two estuaries, had high silicate concentrations during wet seasons (Paudel et al unpublished).

Another explanation for the positive effects of phytoplankton on other dissolved nutrients could be caused by the release of orthophosphate from remineralization. However, the estuaries sediment might have limited the release of orthophosphate by adsorption. The Guadalupe and Nueces Estuaries organic sediment adsorbed all of the supplemented orthophosphate during a 48 hours long laboratory experiment (Paudel unpublished). The indirect effects of environment flow

to both nitrogen and other dissolved nutrients were very weak. That is the reason for the negligible difference in the total and direct effects of environment flow on nitrogen and other dissolved nutrients.

The SEM result implies phytoplankton and environmental flow were the contributors to increase the water turbidity, with phytoplankton having slightly more positive effects than environment flow. The Guadalupe Estuary wet period was accompanied by TSS concentration of more than 100 mg/L (Paudel unpublished), which supports SEM findings of turbidity increases with environmental flow. In the three estuaries water sample TSS was accompanied by phytoplankton during the normal period. The findings of SEM thus support our field observations.

3.5. Conclusion

The present study identified the long term (1987-2012) decrease in dissolved inorganic nitrogen (ammonia and nitrite+nitrate) and orthophosphate concentration in the three South Texas Estuaries. When comparing results obtained from MLR and SEM, TSS has almost negligible effects on dissolved nitrogen, while it has positive effects on dissolved silicate and orthophosphate. Both MLR and SEM showed high importance of chlorophyll-a concentration in the estuaries for the distribution of nitrogen and other dissolved nutrients in the estuaries. Temperature and pH were the significant physical parameters in maintaining inorganic nutrients. Environment flow identified as the most important latent variables to predict inorganic nutrients in the three estuaries. Though MLR did not identify the indirect effects of environment flow, the direct effect of ammonia and nitrite+nitrate concentration with salinity identified by MLR might be conclusive for the significance of flow to maintain inorganic nitrogen in the South Texas Estuaries. Freshwater inflow has maintained the inorganic nutrients in the South Texas Estuaries. The lack of sufficient flow throughout the year in the Nueces Estuary might be the reason for the low inorganic nutrients.

Appendix I

In the present SEM study, exogenous latent measurement model consists of four matrices.

Those were:

- (1) X is a $(q \times 1)$ vector of observable indicator variable of independent latent variable $E1$.

There were three observable indicator variable ($q=3$) i.e., salinity and temperature for latent variable “Environmental flow”; chlorophyll-a for latent variable “Phytoplankton”, described by exogenous latent variables.

$$X = \begin{bmatrix} X1 = Temperature \\ X2 = Salinity \\ X3 = chlorophyll - a \end{bmatrix}$$

- (2) ξ is a $n \times 1$ vector of exogenous latent variables. There were two exogenous latent variables ($n=2$) i.e. “Environmental flow” and “Phytoplankton”.

$$\xi = \begin{bmatrix} \xi1 = environmental\ flow \\ \xi2 = Phytoplankton \end{bmatrix}$$

- (3) δ is a $q \times 1$ vector of error of X , and

$$\delta = \begin{bmatrix} \delta1 \\ \delta2 \\ \delta3 \end{bmatrix}$$

- (4) Λ_x is a $q \times n$ matrix of coefficients relating X to ξ .

$$\Lambda_x = \begin{bmatrix} \lambda1 & 0 \\ \lambda2 & 0 \\ 0 & \lambda3 \end{bmatrix}$$

Similar to exogenous latent measurement model, endogenous latent measurement model also consists of four matrices. Those are:

- (1) Y is a $p \times 1$ vector of indicators of the dependent latent variables n . There are six observable indicators ($p=6$) i.e., secchi and TSS for latent variable “Water Clarity”; NO_{2+3} and NH_3 for latent variable “Nitrogen”; and SiO_4 and PO_4 for latent variable “Other dissolved Nutrients”.

$$Y = \begin{bmatrix} Y1 = secchi \\ Y2 = TSS \\ Y3 = PO_4 \\ Y4 = SiO_4 \\ Y5 = NO_{2+3} \\ Y6 = NH_3 \end{bmatrix}$$

- (2) η is a $m \times 1$ vector of endogenous latent variable. There are four endogenous latent variables ($m=4$) i.e. “Water Clarity”, “Nitrogen”, “Other dissolved Nutrients”, and TSS. TSS was used as indicator variable and endogenous latent variable.

$$\eta = \begin{bmatrix} \eta1 = water\ clarity \\ \eta2 = other\ diss.\ nutrients \\ \eta3 = nitrogen \\ \eta4 = TSS \end{bmatrix}$$

- (3) ε is a $p \times 1$ vector of measurement errors of Y .

$$\varepsilon = \begin{bmatrix} \varepsilon1 \\ \varepsilon2 \\ \varepsilon3 \\ \varepsilon4 \\ \varepsilon5 \\ \varepsilon6 \end{bmatrix}$$

- (4) Λ_y is a $p \times m$ matrix of coefficients relating Y to η .

$$\Lambda_y = \begin{bmatrix} \lambda4 & 0 & 0 & 0 \\ 0 & \lambda5 & 0 & 0 \\ 0 & 0 & \lambda6 & 0 \\ 0 & 0 & \lambda7 & 0 \\ 0 & 0 & 0 & \lambda8 \\ 0 & 0 & 0 & \lambda9 \end{bmatrix}$$

The other three matrices of structural equation for the latent variable model are:

(1) Γ = matrix of coefficients of latent exogenous variables

$$\Gamma = \begin{bmatrix} \gamma_1 & \gamma_2 \\ \gamma_3 & \gamma_4 \\ \gamma_5 & \gamma_6 \end{bmatrix}$$

(2) ζ = is the vector of latent structural errors.

$$\zeta = \begin{bmatrix} \zeta_1 \\ \zeta_2 \\ \zeta_3 \end{bmatrix}$$

(3) B = matrix of coefficients of latent endogenous variable. Because of the absence of cause-effect between water clarity to other dissolved nutrient and nitrogen, and absence of cause-effect relation between nitrogen and other dissolved nutrients, the vector of coefficients from TSS towards latent variables “Nitrogen” and “Other dissolved Nutrients” were used.

$$B = \begin{bmatrix} \beta_1 \\ \beta_2 \end{bmatrix}$$

In the model the associated covariance matrices' the off-diagonal elements are zero. And following are the covariance matrices:

(1) θ_δ = covariance between measurement errors in X.

$$\theta_\delta(q \times q) = \begin{bmatrix} \text{Var}\delta_1 & & \\ 0 & \text{Var}\delta_2 & \\ 0 & 0 & \text{Var}\delta_3 \end{bmatrix}$$

(2) θ_ϵ = covariance between measurement errors in Y.

$$\theta_\epsilon(p \times p) = \begin{bmatrix} \text{Var}\epsilon_1 & & & & & \\ 0 & \text{Var}\epsilon_2 & & & & \\ 0 & 0 & \text{Var}\epsilon_3 & & & \\ 0 & 0 & 0 & \text{Var}\epsilon_4 & & \\ 0 & 0 & 0 & 0 & \text{Var}\epsilon_5 & \\ 0 & 0 & 0 & 0 & 0 & \text{Var}\epsilon_6 \end{bmatrix}$$

(3) Ψ = covariance between structural errors i.e. of $m \times m$. Here, Ψ_{11} is “water clarity”, Ψ_{22} is “other dissolved nutrients”, Ψ_{33} is “Nitrogen”, and Ψ_{44} is “TSS”.

$$\Psi (m \times m) = \begin{bmatrix} \Psi_{11} & & & \\ 0 & \Psi_{22} & & \\ 0 & 0 & \Psi_{33} & \\ 0 & 0 & 0 & \Psi_{44} \end{bmatrix}$$

(4) Φ = covariance between the independent variable. Here Φ_{11} is “environmental flow’ and Φ_{22} is “phytoplankton”.

$$\Phi (n \times n) = \begin{bmatrix} \Phi_{11} & \\ 0 & \Phi_{22} \end{bmatrix}$$

The metric of one loading in each column of Λ_x and Λ_y were fixed to 1. The latent variable phytoplankton has one indicator and that loading was fixed to 1. In the present study we assumed following $\lambda_1 = \lambda_4 = \lambda_5 = \lambda_7 = \lambda_9 = 1.0$.

Following are the model configuration for the SEM:

$$(X_1)\text{Temp} = \lambda_1 \xi_1 + \delta_1,$$

$$(X_2)\text{Sal} = \lambda_2 \xi_1 + \delta_2,$$

$$(X_3)\text{Chlorophyll-a} = \lambda_3 \xi_2 + \delta_3,$$

$$(Y_1)\text{Secchi} = \lambda_4 \eta_1 + \varepsilon_1,$$

$$(Y_2)\text{TSS} = \lambda_5 \eta_1 + \varepsilon_2,$$

$$(Y_3)\text{PO}_4 = \lambda_6 \eta_2 + \varepsilon_3,$$

$$(Y_4)SiO_4 = \lambda_7\eta_2 + \varepsilon_4,$$

$$(Y_5)NO_{2+3} = \lambda_8\eta_3 + \varepsilon_5,$$

$$(Y_6)NH_3 = \lambda_9\eta_3 + \varepsilon_6,$$

$$\eta_1 = \gamma_1\xi_1 + \gamma_1\xi_2 + \zeta_1,$$

$$\eta_2 = \gamma_4\xi_1 + \gamma_6\xi_2 + \beta_1 \eta_4 + \zeta_2,$$

$$\eta_3 = \gamma_3\xi_1 + \gamma_5\xi_2 + \beta_2 \eta_4 + \zeta_3,$$

After the model parameter were specified, the model covariance matrix was identified by using conditional covariance matrix specified by given by Bollen (1989), i.e.

$$\Sigma(\theta) = \begin{bmatrix} \Lambda y(I - B)^{-1}(\Gamma\Phi\Gamma' + \Psi)(I - B)^{-1}\Lambda y' + \theta_\varepsilon & \Lambda y(I - B)^{-1}\Gamma\Phi\Lambda x' \\ \Lambda x\Phi\Gamma'(I - B)^{-1}\Lambda y' & \Lambda x\Phi\Lambda x' + \theta_\delta \end{bmatrix}$$

Thus $\Sigma(\theta)$ will be yielded.

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CHAPTER IV

EFFECT OF SEDIMENT ORGANIC MATTER AND MINERAL CONTENT ON THE RELEASE OF SILICATE AND ORTHOPHOSPHATE ALONG A SALINITY GRADIENT.

Abstract

During a long-term study (1987-2013), we found dissolved silicate and orthophosphate concentrations had non-conservative mixing behavior in the Guadalupe and Nueces Estuaries. To explain this behavior it was hypothesized that sediment organic matter, sediment minerals and pore water chemistry influenced the non-conservative behavior. An experiment was performed to measure nutrient release from sediments with and without organic content from the Guadalupe and Nueces Estuaries at five different salinities. The sample mixtures were shaken at intervals over the course of 48 hours to simulate wind and river forcing. The release of silicate from sediments increased with time from 2 minutes to 48 hours in the zero salinity solutions; however, the silicate release was less at higher salinities. The added orthophosphate concentration was adsorbed in most of the sediment containing organic matter from both estuaries. In the treatment without organic matter, the release of orthophosphate from the sediments was as high as 52 $\mu\text{mol/L}$. Quartz and calcite were abundant in sediment samples from both estuaries. The average quartz to corundum peak intensity ratios were 14.04 and 13.36 and the average calcite to corundum peak intensity ratios were 3.06 and 1.32 in the Guadalupe and Nueces Estuaries, respectively. The retention and release of orthophosphate from the sediments may have been caused by the binding with organic matter and calcite in the sediments. These findings indicate

that sediment organic matter was a significant contributor in the low dissolved orthophosphate concentration in the estuaries. The release of silicate from the sediments containing quartz and organic matter, when shaken, indicate that the combined forcing of river current and wind may have been maintaining the estuaries silicate concentrations.

Key Words: Silicate, Orthophosphate, Quartz, Calcite, Organic matter.

4.1. Introduction

The non-conservative behavior of dissolved silicate and phosphate along estuarine salinity gradients might be due to the interaction between sediment composition and overlying water (Anderson 1986; Morris et al. 1981; D'Elia et al. 1983). The sediment composition includes sediment content of organic matter and minerals that interact in the presence of salt water electrolytes. This, in turn, may affect retention-release, precipitation-dissolution and flocculation-deflocculation of dissolved silicate and phosphate.

According to previous studies, transported dissolved silicate concentration decreases as it moves from a river to an estuary along a salinity gradient (Conley 1992; Morris et al. 1981; Eyre and Balls 1999). Several explanations have been suggested for the decrease in silicate along the river-mouth to estuary-ocean salinity gradients. These include coagulation of a colloidal form of silica (Krauskopf 1956), retention of silicate on clay minerals as it moves from freshwater to the saltwater interface (Williams and Crerar 1985), and silicate uptake by diatoms (Conley 1992). A sudden increase in silicate concentration in oligohaline (salinity 0.5-5 ppt, Venice Classification system; Anonymous 1958) regions from riverine concentrations, may be a result of the dissolution of biogenic silica present in river water (Anderson 1986).

Previous studies have revealed two types of phosphate behavior caused by estuarine salinity gradients. The first one is the sudden decrease in dissolved phosphate concentration from fresh to saline water gradients with most of the losses at the confluence of a river and an estuary. There are several potential causes of this sudden decrease in concentration; a change in pH (Garcia 2006), precipitation of phosphate-colloid (Bale and Morris 1981), and retention of phosphate onto suspended clay particles (Garcia 2006). The second type of phosphate behavior was the

increase in phosphate concentration in oligohaline regions because of the release of phosphorus from the iron and aluminum oxide organic complex as the river water mixes with the estuary water (Sundareshwor and Moris 1999). Flocculation of organic matter inhibits release from organic complexes as sediment is transported to mesohaline (salinity 5-18 ppt, Venice Classification system; Anonymous 1958) and polyhaline (salinity 18-30 ppt, Venice Classification system; Anonymous 1958) regions, and results in a decrease in phosphate concentration in the oceanic end of an estuary (Howarth et al. 1985; Nielson et al. 2001).

Recent research has found a 35 ppt salt solution can dissolve silica gel and release silicate into the water (Tanaka and Takahashi 2013). Additionally, Spagnoli and Bergamini (1997) identified the release of phosphate during resuspension. The interaction between sediment composition and water in the estuaries may have a significant role in the retention and release of silicate and orthophosphate from the sediment. There were high values of silicate and orthophosphate concentrations at salinities greater than 25 ppt in the Guadalupe and Nueces Estuaries (Paudel B unpublished). Another weekly nutrient study in Nueces and Corpus Christi Bay identified short term removal of orthophosphate concentrations, and high silicate concentration at salinities greater than 20 ppt (B. Paudel unpublished work). In the Guadalupe and Nueces Estuaries, salinity variation and resuspension induced by wind or river flow may be the major factors that cause variation in sediment nutrient release. Therefore it is important to identify the effects of estuarine sediment composition at various salinities and the retention and release of silicate and orthophosphate concentrations due to resuspension. The main objectives of the present study were 1) to identify long term (1987-2013) trends of dissolved silicate and orthophosphate concentrations along salinity gradients in the Nueces and Guadalupe Estuaries and 2) to characterize silicate and orthophosphate release from sediment in a laboratory setting

by varying sediment organic matter, salinity and agitation rate. Agitation was used to mimic river flow and wind forcing.

4.2. Materials and Methods

4.2.1. Long term water sample collection

Long-term silicate and orthophosphate data from Guadalupe and Nueces Estuaries were used for this study (Table 4.1). The dataset consists of dissolved silicate and orthophosphate concentrations from the surface and 20 cm above the bottom at four stations in the Guadalupe Estuary and five stations in the Nueces Estuary, taken every quarter (January, April, July, and October) from 1987 to 2013. Details on sample collection, location of each station in the estuary, measured water quality parameters and method of collection are provided in several publications (Montagna and Kalke 1992; Kim and Montagna 2012). From here on, all field results refer to the long-term study, except where mentioned otherwise.

4.2.2. Sediment sample collection sites

The top 5 cm of sediment were collected using cores from station ‘A’ of Guadalupe and Nueces Estuaries during July 2012, October 2012, and January 2013 (Fig. 4.1). Data collected from station A of both estuaries were used because the location was closer to the river mouth, and was therefore assumed to have higher organic loads. In the field, sediment samples were kept on ice and stored frozen upon transfer to the lab in order to slow organic matter degradation. Organic contents, mineral contents and nutrient release experiments were performed using these sediment samples.

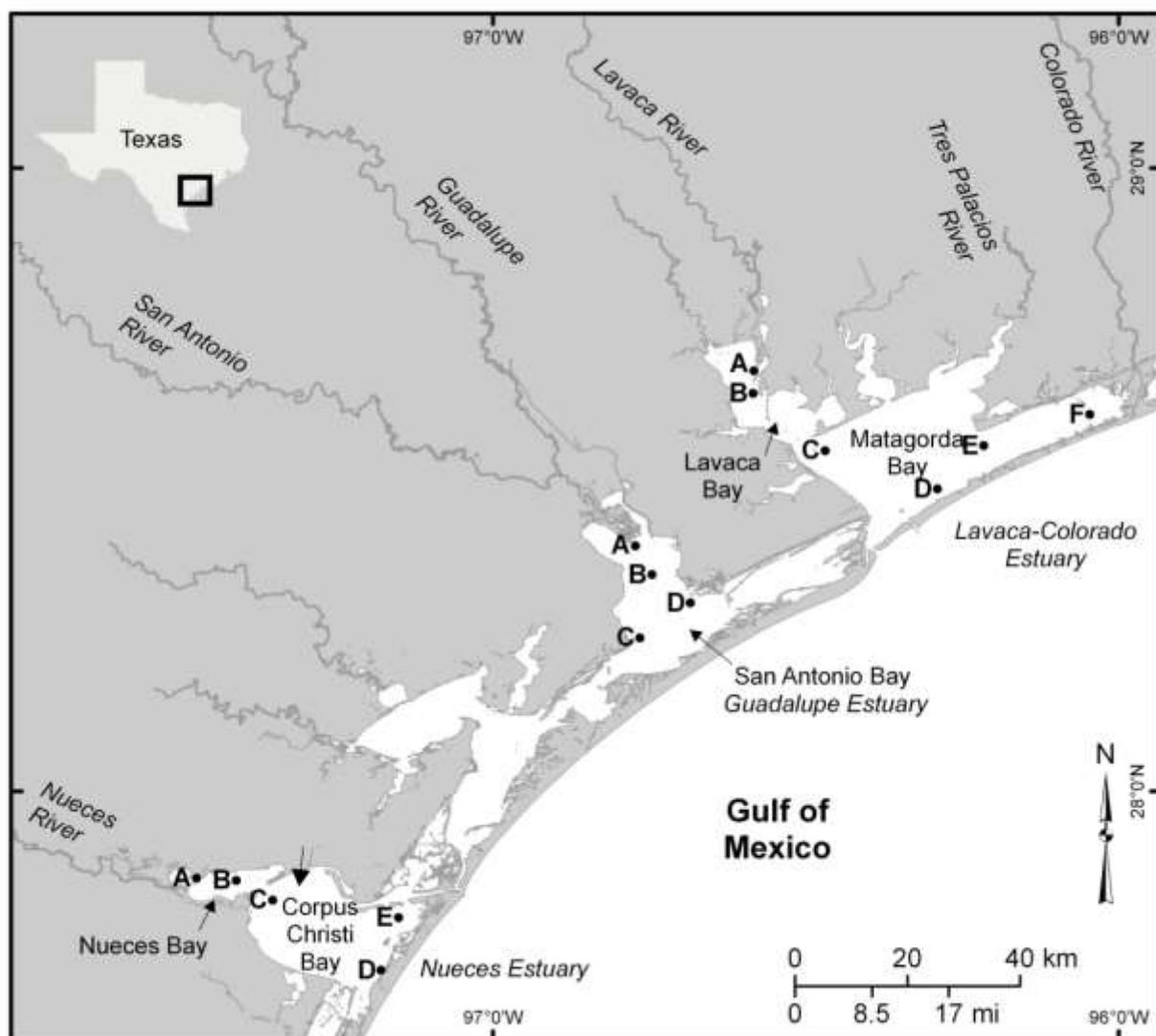


Fig. 4.1. Map of Study sites with stations

4.2.3. Sediment analysis and laboratory experiments

The laboratory experiments were conducted at room temperature to avoid any possible effect of temperature on sediment silicate and orthophosphate release. Before the sediment was used for laboratory experiments, organic matter, and mineral analyses, it was carefully homogenized.

4.2.3.1. Organic matter

The organic matter content in the sediment sample was determined by H_2O_2 digestion (Schumacher, 2002). A 10 – 15 g sediment sample was weighed and dried overnight at 60 °C in an aluminum pan. After drying, the samples were reweighed and each placed in a beaker containing 50 ml of 30 % H_2O_2 . The sediment was allowed to digest until effervescence stopped. After the digestion of organic matter the supernatant was decanted and an aliquot of deionized (DI) water was added. The beaker was stirred and allowed to settle until the supernatant was clear. This process was repeated two more times. The sample was then filtered by pouring the beaker contents through a 0.7 μm filter paper suspended in a glass funnel. The sediment collected on the filter paper was oven dried at 60 °C overnight. The samples were again weighed. Sediment organic matter was calculated by the difference in weight before and after organic matter digestion.

4.2.3.2. Mineral composition

Sediment samples without organic matter was ground using a mortar and pestle, and 2 g of sample was mixed with 0.5 g of corundum ($\alpha\text{-Al}_2\text{O}_3$) in a 4:1 ratio (Naehr et al., 2000). A few drops of ethyl alcohol were added to the sample-corundum mixture to help with homogenization of the mixture. Then each prepared sample was placed in a sample holder of a Rigaku Ultima III

X-ray diffractometer and sediment mineral composition was identified. Scans were run from 2° to $80^{\circ} 2\theta$ with scanning speed of $0.01^{\circ} 2\theta/s$. The crystal structure of each mineral is composed of set of planes responsible for 'd' values (distance between array of crystal in mineral), and which is responsible for the variations in the peak. The obtained peak was compared with a known standard peak to determine the mineral types. The peak, obtained as intensity count per second of the mineral type was compared with the corundum peak, and the mineral content identified based on the mineral to corundum ratio. MDI Jade-7 software (Bishop et al., 2011) was used to identify mineral types and peak intensities. The software can automatically identify the mineral content in the sample based on the location of the peak. However, the user has to differentiate the mineral type based on the 'd' value and one main peak of the mineral.

4.2.3.3. Preparation of a nutrient spike solution

Primary standards with a concentration of $10,000 \mu\text{mol/L}$ were prepared for each analyte of concern using oven dried (105°C) potassium nitrate (KNO_3), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), and potassium phosphate monobasic (KH_2PO_4), as well as undried sodium metasilicate pentahydrate (Na_2SiO_3) and potassium nitrite (KNO_2). Each chemical was weighed, placed in 1000 mL volumetric flasks and brought up to 1000 ml with freshly drawn Milli-Q water. From these refrigerated primary standards, a 100 mL mixed stock standard was prepared daily containing $250 \mu\text{mol/L NO}_2$, $250 \mu\text{mol/L NO}_3$, $500 \mu\text{mol/L NH}_4$, $500 \mu\text{mol/L PO}_4$, and $5000 \mu\text{mol/L SiO}_2$. This solution was then used to "spike" the sediment with additional nutrients in the following experiments.

4.2.3.4. Experimental design for laboratory study

All the laboratory experiments to identify sediment nutrient release were performed within two weeks of sample collection. The laboratory experiments were conducted using sediments with and without organic matter treatments at five salinity solutions over a period of 48 hours. A total of 6 laboratory experiments (3 with organic + 3 without organic matter) using sediments from the Nueces Estuary and 6 laboratory experiments (3 with organic + 3 without organic matter) using sediments from the Guadalupe Estuary sediment samples were conducted (Fig. 4.2). Five salinity solutions of 0 (DI water), 7.5, 15, 25, and 35 ppt were prepared using low nutrient seawater (LNSW) and DI water. During each experiment, the sediment to solution ratio was set to 1:30 by mixing 4 g of sediment with 120 ml of solution in a 250 ml Erlenmeyer flask. The experiment was conducted with two replicates for each salinity solution from both estuaries for a total of 20 flasks. Each flask was supplemented with the spike nutrient solution to provide an additional concentration of 5 $\mu\text{mol/L}$ of NH_4 , 5 $\mu\text{mol/L}$ of PO_4 , 5 $\mu\text{mol/L}$ of NO_{2+3} and 50 $\mu\text{mol/L}$ of SiO_4 .

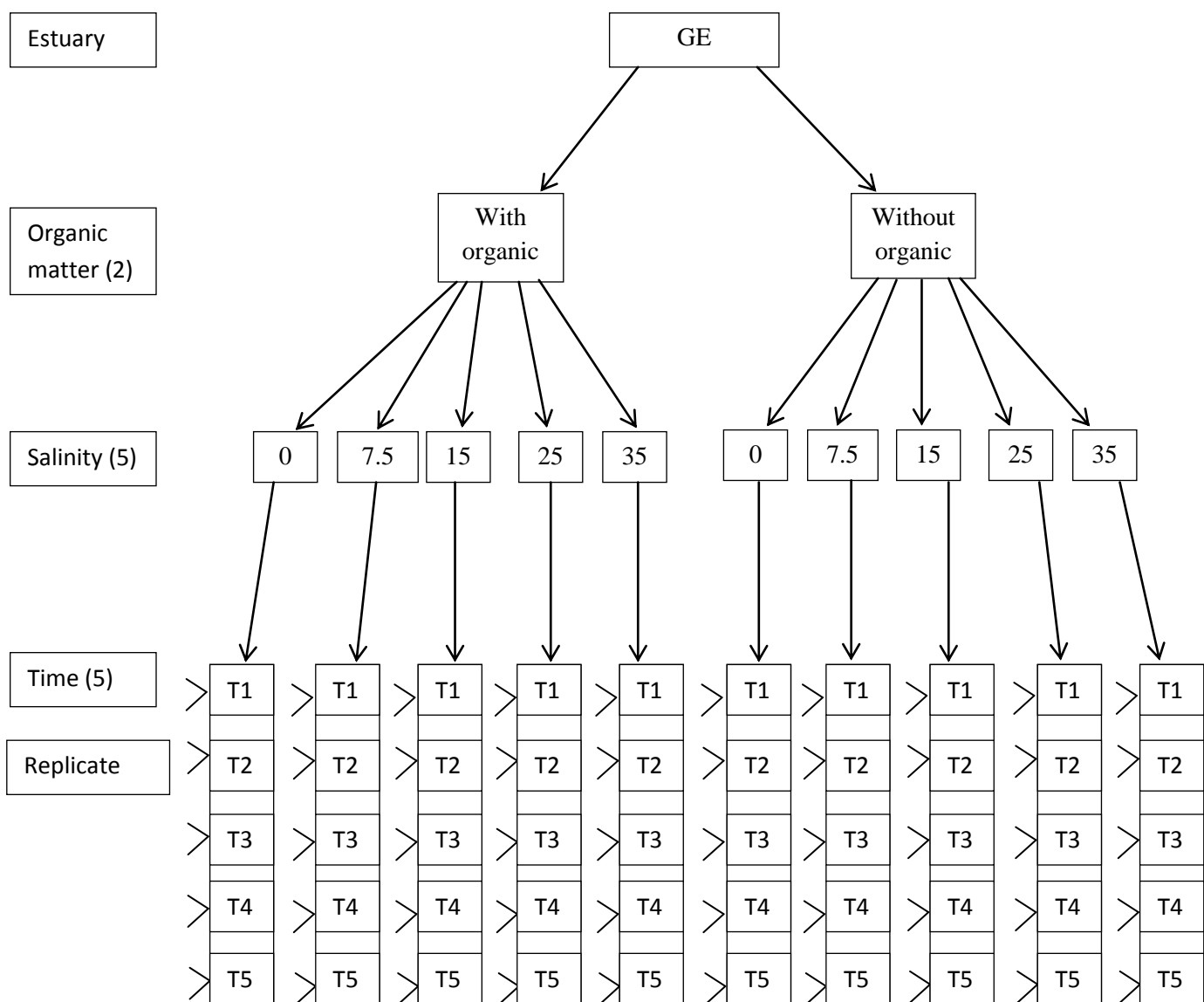


Fig. 4.2. Experimental Design for the laboratory experiment, only Guadalupe Estuary (GE) is showing. Design repeated for Nueces Estuary (NC).

T1 = 1min, T2 = 15 mins, T3 = 50 mins, T4 = 360 mins, T5 = 48 hrs,

> = replicates

The spiked salinity solutions were carefully mixed prior to adding the weighed sediment to each flask. After sediment addition, a 25 ml sample was collected from each flask, using a large bore plastic syringe, to be used as the baseline measurement (T_1). Additional water samples for nutrient analysis were then collected at 10 mins (T_2), 50 mins (T_3), 360 (T_4) mins and 48 hours (T_5) after the addition of sediment to the flasks. The flasks were shaken vigorously using an oscillating shaker between each sampling time. The samples were shaken for approximately 50 seconds at the following intervals: every 2 mins between T_1 to T_2 , every 5 mins between T_2 to T_3 , every 15 mins between T_3 to T_4 and every hour between T_4 to T_5 . The samples were allowed to settle for 10 hours overnight and the agitation protocol was resumed the following day.

A control was prepared using the nutrient spike solution at the same salinity and nutrient concentration as in the experimental flasks but without the sediment addition. The control was designed to identify and measure the degradation of nutrients in the solutions over time without sediment influence.

4.2.3.5. Inorganic nutrient analyses

Nutrient samples were taken from each Erlenmeyer flask using 25 ml syringes and each was filtered through 0.45 μm filter paper. Each sample was kept frozen in a labeled, 12-ml vial until analysis. An O.I Segmented Flow Autoanalyzer was used for nutrient analysis. The lowest detection limit for silicate and orthophosphate concentrations used to prepare standard curve were 5 and 0.25 $\mu\text{mol/L}$, respectively.

4.2.4. Statistical method

Multivariate analysis of variance (MANOVA) was performed to identify the effects of salinity (SAL), time, organic matter content (OM) and estuaries (EST) on silicate and orthophosphate concentration. Before the analysis, silicate and orthophosphate data were log transformed. MANOVA and ANOVA were performed using PROC GLM procedure in SAS (Version 9.2). The model tested in SAS was: $\text{SIO}_4 \text{ PO}_4 = \text{EST} \mid \text{OM} \mid \text{SAL} \mid \text{TIME}$; where: EST = Estuaries, OM = Organic matter, SAL = salinity.

All graphs were created using SAS. The PROC SGSCATTER and PROC COMPARE procedure was performed to compare different variables. PROC GCHART was performed to get bar diagrams and PROC GREPLAY was used to obtain a panel of different bar diagrams.

4.3. Results

4.3.1. Silicate and Orthophosphate concentrations in the Nueces and Guadalupe Estuaries

A decrease in dissolved silicate (SiO_4) concentrations along a salinity gradient was identified in the Guadalupe and Nueces Estuaries (Table 4.1, Figs. 4.3 and 4.4). However, non-conservative behavior of SiO_4 was identified along the salinity gradient in both estuaries. In the Guadalupe Estuary, surface water SiO_4 concentrations were higher at the river-estuary mouth, where salinity ranged from 0 to 4 ppt, compared to the higher salinity areas within the estuary. In the Nueces Estuary, most of the higher SiO_4 concentrations greater than 150 ($\mu\text{mol/L}$), occurred at 20 ppt or greater. The theoretical dilution line was plotted by calculating the average silicate and orthophosphate concentration at 0 and 35 ppt salinities in the Guadalupe Estuary. In the Guadalupe Estuary, average zero salinity silicate and orthophosphate concentrations were 185.78 $\mu\text{mol/L}$ and 3.49 $\mu\text{mol/L}$, respectively. In the Nueces Estuary, 0 salinity silicate and orthophosphate concentrations were not found so the Guadalupe Estuary 0 salinity data were used to plot a theoretical dilution line.

Table 4.1 Locations and average salinity, phosphate and silicate concentrations for the long-term field stations. Abbreviations: N = number of samples, PO4 = phosphate, SiO4 = silicate, and SE = standard error.

Estuary	Station	Latitude	Longitude	N	Salinity (ppt)		PO4 (umol/L)		SiO4 (umol/L)	
					mean	(SE)	mean	(SE)	mean	(SE)
GE	A	28.36878	-96.71878	249	9.17	(0.62)	3.26	(0.19)	152.17	(8.58)
GE	B	28.37248	-96.72080	262	13.47	(0.64)	2.14	(0.14)	131.13	(6.88)
GE	C	28.31027	-96.68002	245	18.32	(0.73)	1.68	(0.11)	106.49	(6.01)
GE	D	28.31397	-96.67832	259	19.21	(0.72)	1.46	(0.10)	97.91	(4.14)
NC	A	28.39352	-96.77240	263	25.11	(0.76)	1.92	(0.07)	118.96	(4.82)
NC	B	28.34777	-96.74573	260	29.49	(0.56)	1.23	(0.06)	82.07	(3.99)
NC	C	28.24618	-96.76488	270	31.55	(0.36)	0.60	(0.03)	46.48	(2.59)
NC	D	28.30210	-96.68435	262	32.86	(0.37)	0.52	(0.05)	43.82	(2.39)
NC	E	28.35137	-96.70798	248	31.66	(0.34)	0.46	(0.03)	41.43	(2.40)

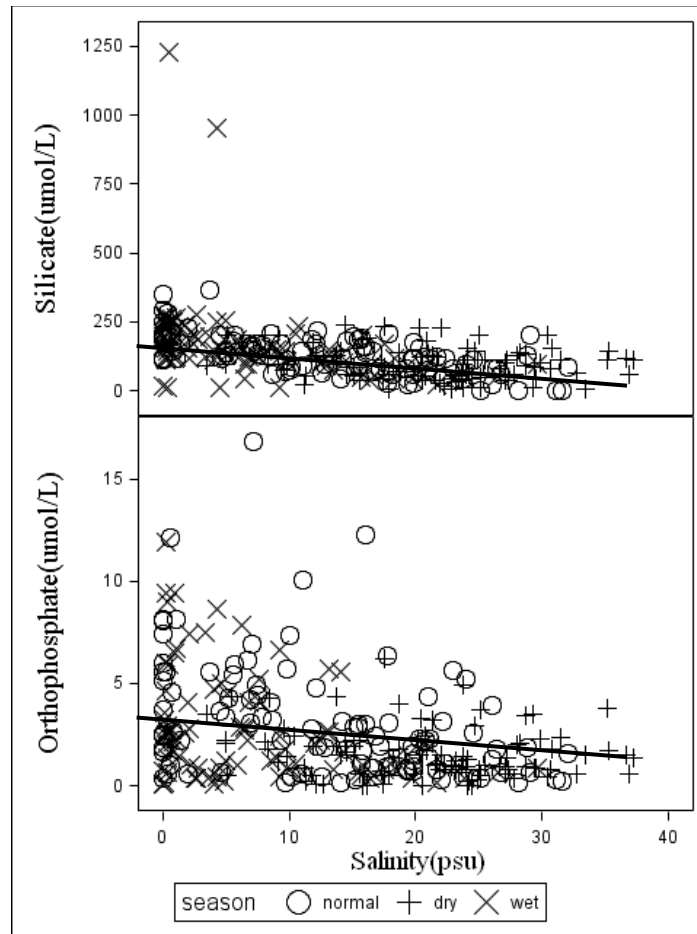


Fig. 4.3 Long-term (1987 – 2013) Guadalupe Estuary wet, dry, and normal period's silicate and orthophosphate concentrations. The straight line in the figure indicates the theoretical dilution line along salinity gradients.

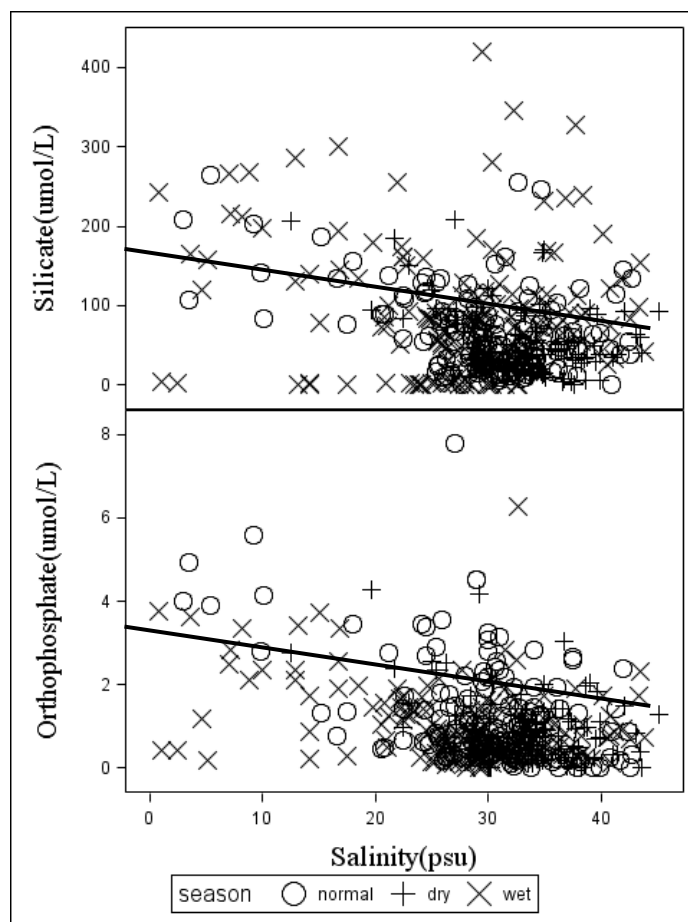


Fig. 4.4 Long-term (1987 – 2013) Nueces Estuary wet, dry, and normal period's silicate and orthophosphate concentrations. The straight line in the figure indicates theoretical dilution line along salinity gradients.

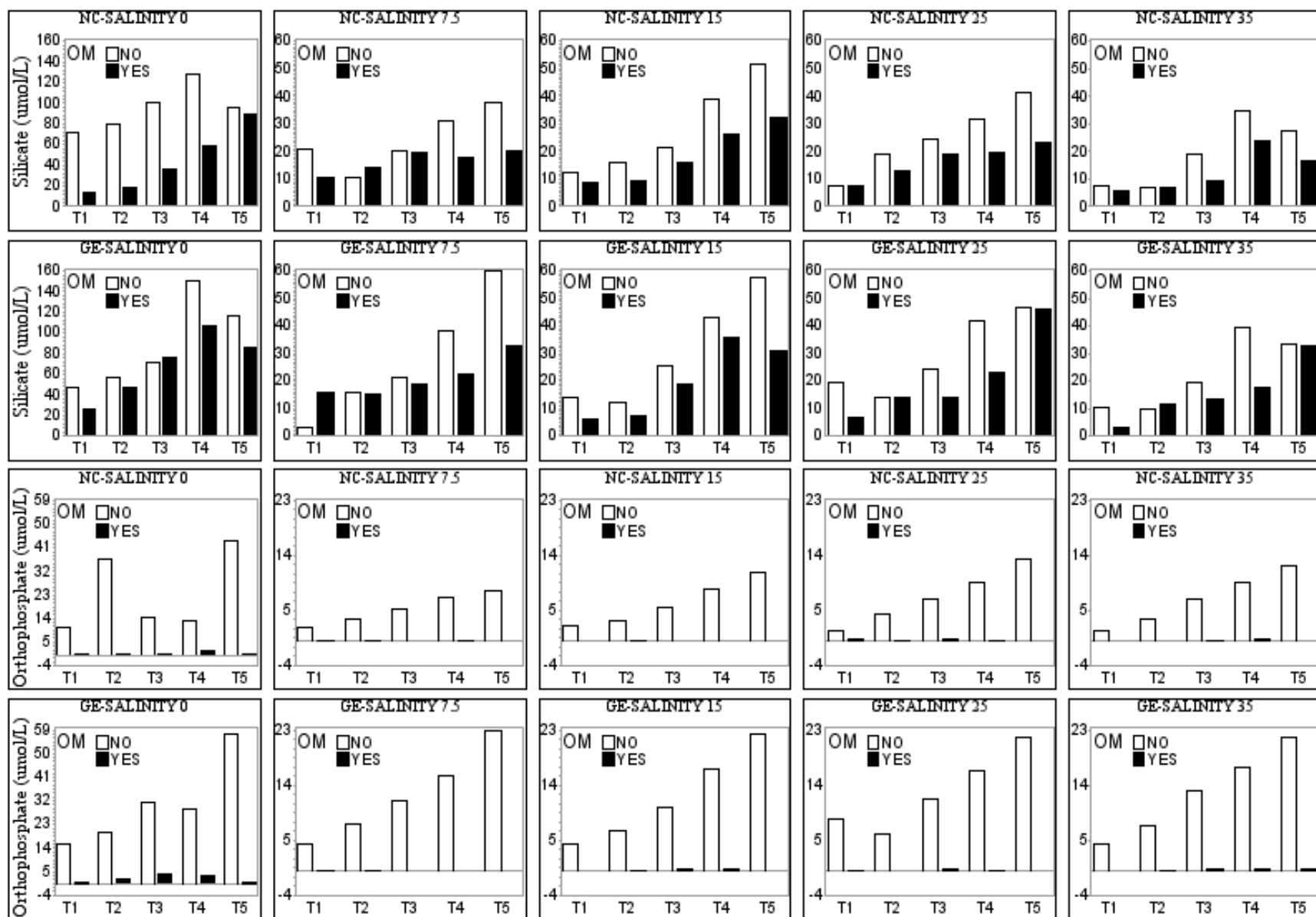


Fig. 4.5 Average silicate and orthophosphate release from sediments with and without organic treatments of the Guadalupe (GE) and Nueces (NC) Estuaries samples at different salinities. Y-axes of 1st and 2nd rows of the figure are silicate concentrations and Y-axes of 3rd and 4th rows are orthophosphate concentrations. OM= Organic matter (NO indicates treatments without organic matter after H₂O₂ digestion; YES indicates treatments with organic matter)

Table 4.2 ANOVA result to determine the difference in silicate and orthophosphate concentrations by different source variables. Abbreviations: Est = Estuary, OM = organic matter, Sal = salinity.

Variable	Source	P-value
Orthophosphate	Est	<0.0001*
	OM	<0.0001*
	Time	<0.0001*
	Sal	<0.0001*
Silicate	Est	0.2084
	OM	<0.0001*
	Time	<0.0001*
	Sal	<0.0001*

* denotes significant values

The orthophosphate (PO_4) concentrations behaved non-conservatively as did the SiO_4 concentrations along the salinity gradients of the Guadalupe and Nueces Estuaries. Similar to SiO_4 in the Guadalupe Estuary and the Nueces Estuary, orthophosphate was higher at the river mouth compared to the higher salinity regions. In the Guadalupe Estuary, most of the orthophosphate concentrations were less than 5 $\mu\text{mol/L}$, whereas in the Nueces Estuary most concentrations were less than 2 $\mu\text{mol/L}$ (Fig. 4.3 and 4.4). In estuaries, high silicate and orthophosphate concentrations were observed at high salinity, i.e. above 20 ppt.

4.3.2. Silicate and Orthophosphate concentrations in laboratory experiments

In the lab, SiO_4 concentration was highest in the treatments without sediment organic matter. The difference in SiO_4 concentration between Time-T5 and Time-T1 was higher in the DI treatments without sediment organic matter compared to salinity treatments without sediment organic matter. The average highest SiO_4 concentrations of 120 $\mu\text{mol/L}$ from the Nueces Estuary and 140 $\mu\text{mol/L}$ from the Guadalupe Estuary were observed in the DI treatments without sediment organic matter at Time-T4. There was a sharp decrease in SiO_4 concentration from 0 to 7.5 ppt in both experiments with and without sediment organic matter (Fig. 4.5). The concentration of SiO_4 was significantly different with respect to time, salinity, and organic content as variables, whereas it was not significantly different between the two estuaries (Table 4.2). Additionally the SiO_4 concentrations were affected more with time and less with organic matter and salinity. The dissolved orthophosphate (PO_4) concentrations in all saline treatments with sediment organic matter were below detection levels regardless of time. However, the PO_4 in some DI treatments with sediment organic matter did show detectable levels of PO_4 . Four out of ten average orthophosphate concentrations in the DI treatments with sediment organic matter

were greater than 0 $\mu\text{mol/L}$, i.e. ranged from 0.6 to 2.7 $\mu\text{mol/L}$, of which only one was from the Nueces Estuary treatment. The average orthophosphate concentration was the highest in the DI treatments without organic matter. The average concentration identified in the DI treatments without sediment organic matter from the Nueces Estuary and the Guadalupe Estuary were 24.1 and 30.2 $\mu\text{mol/L}$ respectively (Fig 4.6 and 4.7). In the saline treatments without organic matter, the orthophosphate concentration was higher in the Guadalupe Estuary treatments compared to the Nueces Estuary treatments (Fig 4.5). The orthophosphate concentrations in the treatments without organic matter in all salinities increased over time (Fig. 4.5). The PO_4 concentrations were significantly different with respect to organic matter, time, salinity, and estuary (Table 4.2).

4.3.3. Sediment mineral and organic composition

In both estuaries, quartz was the dominant mineral based on the mineral to corundum ratio. The average quartzite to corundum ratio was 14.04 and 13.86 in the Guadalupe and Nueces Estuaries, respectively (Fig. 4.8). Besides quartzite (SiO_2), calcite (CaCO_3) and feldspar were also found in the sediments. Calcite was higher in the Guadalupe Estuary than in the Nueces Estuary, i.e., the average calcite to corundum ratio was 3.06 and 1.32 in the Guadalupe and Nueces Estuaries, respectively (Fig. 4.8). In most of the samples, magnesium carbonate (MgCO_3) was less than 2% of Mg/Ca in carbonate minerals.

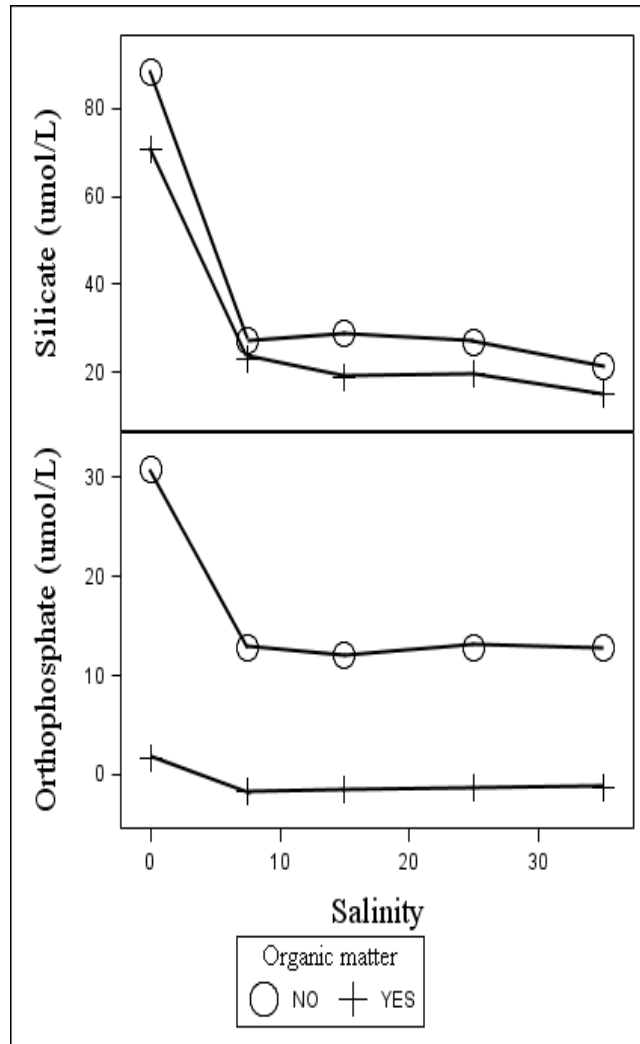


Fig. 4.6 Release of average silicate and orthophosphate concentration from the Guadalupe Estuary's with and without organic treatments.

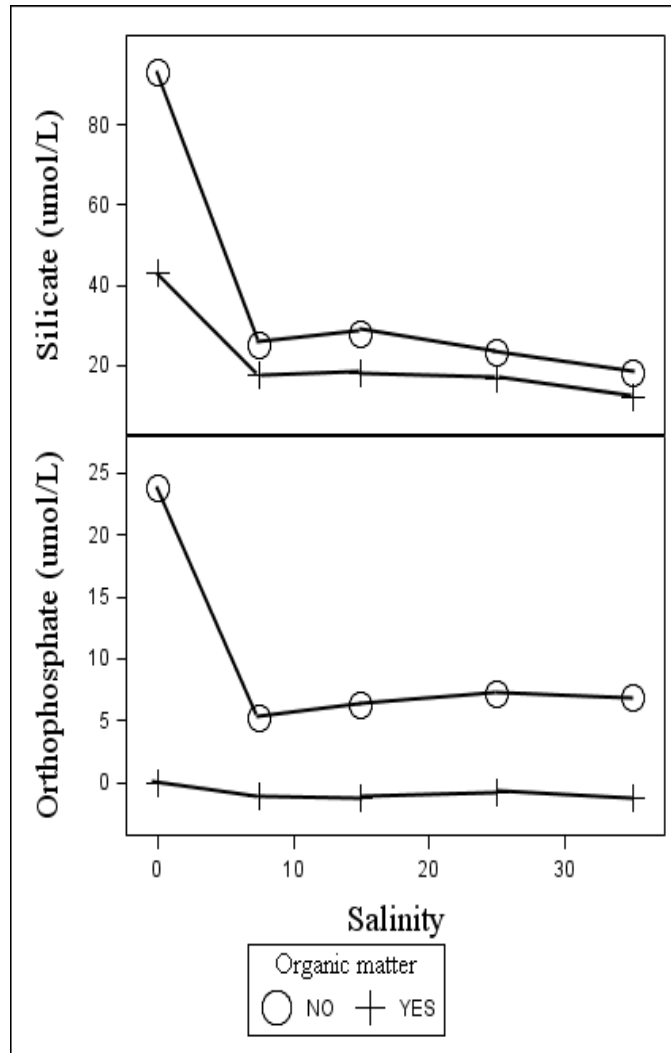


Fig. 4.7 Release of average silicate and orthophosphate concentration from the Nueces Estuary's with and without organic treatments.

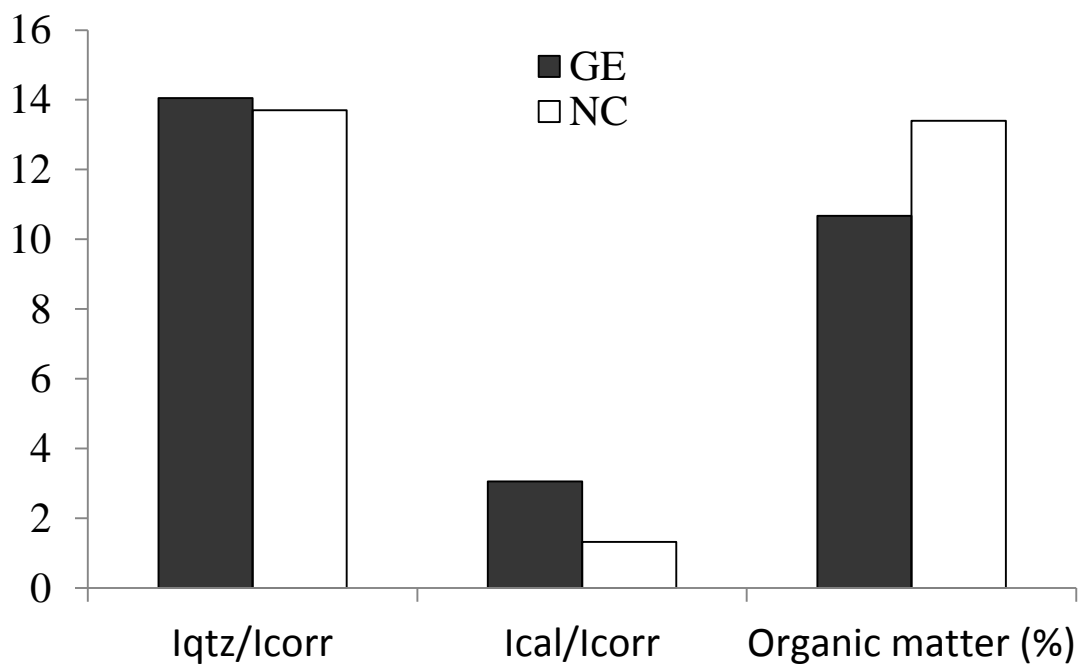


Fig. 4.8 Sediment mineral and organic matter content in the Guadalupe (GE) and Nueces (NC) Estuaries.

Abbreviations: Iqtz = peak intensity count per second of quartz, Icorr = peak intensity count per second of corundum (Al_2O_3), Ical = peak intensity count per second of calcite

The organic matter contents in the Guadalupe and Nueces Estuary were almost the same in the July 2012 and January 2013 samples, however, the organic matter content in the October 2012 Guadalupe Estuary's sediments (3.87%) was significantly less than that of the Nueces Estuary's sediments (13.84%). The average organic matter content in the Nueces Estuary was greater than in the Guadalupe Estuary (Fig. 4.8).

4.4. Discussion

4.4.1. Dissolved silicate in the estuary and in the laboratory

In the Guadalupe Estuary most of the high SiO_4 concentrations were clustered in low salinity regions, whereas in the Nueces Estuary the majority of the SiO_4 concentrations were observed at salinities greater than 25 ppt. The major difference identified in the distribution of the Guadalupe and Nueces Estuaries' SiO_4 concentration might be due to the difference in freshwater inflow, with the Guadalupe estuary receiving more inflow (Montagna et al. 2013; Palmer et al. 2011).

The SiO_4 concentrations in the Guadalupe and Nueces Estuaries decreased along the river-estuary to the tidal-inlet salinity gradients, however there were concentrations below and above the theoretical dilution line (Fig. 4.3 and 4.4). In the lab experiment with and without organic sediments, the SiO_4 concentration decreased sharply from 0 to 7.5 ppt and then remained almost constant from 7.5 to 35 ppt (Fig. 4.6 and 4.7). Previous studies have found a positive correlation between SiO_4 and NaCl , Na_2SO_4 and NaNO_3 , the major components of sea water, until the concentration of NaCl and NaNO_3 reaches 1 M (equivalent to 35 ppt). Beyond 1 M only Na_2SO_4 showed a positive correlation (Tanaka and Takahashi 2005; Tanaka and Takahashi 2007). The decrease in solubility of silicate along the salinity gradients might not be the reason for the decrease in SiO_4 concentration. Rather, the field and lab results indicate the estuaries' sediment is the source and sink for silicate and orthophosphate.

Past studies have suggested that a decrease in SiO_4 from a river water concentration along the increasing estuary salinity gradient might be due to the adsorption of colloidal silicates to clay particles suspended in the water column (Liss and Spencer 1970; Morris et al. 1981). The dense

turbidity observed in the sediment-DI water mixture compared to that of the sediment-7.5 ppt and 35 ppt mixtures, after 1 hour of sample shaking, indicates particulates settled faster in the saline solutions than in the zero salinity solution. The particulate and colloidal silicate might have precipitated with the settled particulate matter in the saline solutions. The adsorption of SiO_4 on sediment minerals, or precipitation of particulate and colloidal silicates in the salt water, may be the possible explanation for the decrease in SiO_4 concentration in the salinity gradient.

The average river water SiO_4 concentration is about 150 $\mu\text{mol/L}$ (Conley 1997), while average zero salinity SiO_4 concentration in the Guadalupe Estuary was 185.78 $\mu\text{mol/L}$. The SiO_4 concentration of 125 $\mu\text{mol/L}$ was observed at a salinity of 25 ppt and greater in the 2010-2013 study of Nueces and Guadalupe Estuaries. Additionally, a 125 $\mu\text{mol/L}$ SiO_4 concentration at salinities greater than 25 ppt was also found in the long-term study of both estuaries. The high dissolved silicate concentration might be due to the interaction between water and sediment components. Wind-induced resuspension and salinity-induced dissolution may affect the interaction between sediment and overlying water resulting in an increase in the SiO_4 concentration. In the lab, the SiO_4 concentration was higher in the freshwater solutions compared to that of the saline solutions. Most of the SiO_4 concentrations decreased with salinity increase; however, in a few samples the SiO_4 concentrations observed at 25 ppt were higher than those observed at 15 ppt. The reason for this increase was not identified. The SiO_4 concentration increased from time-T1 to time-T5 in all five salinity solutions (Fig. 4.5). The increase in SiO_4 concentrations over time in the experiments may indicate that shaking the samples released additional SiO_4 . Past study has found that resuspension in some estuaries can release silicate from sediment containing silicate minerals (Rickert 2000; Rickert et al. 2002). The present study showed that sample agitation, in an attempt to mimic wind forcing and river flow, resulted in

resuspension and may have released silicate concentrations equivalent to those found in river water.

Sediment mineralogy analyses performed in the lab demonstrated that quartz and calcite are the major minerals found in sediments of the Guadalupe and Nueces Estuaries. The concentrations of quartz were similar in both estuaries; however, calcite concentration was higher in the Guadalupe Estuary (Fig. 4.8). Feldspar was detected in small amounts in some sediment samples, but not all. The presence of quartz in the Guadalupe and Nueces Estuaries could be the reason for the high silicate concentration in most of the field and lab samples. Past studies have found that at ordinary room temperature the solubility of amorphous silica can be as high as 100 ppm while the solubility of quartz is around 6 ppm (Krauskopf 1956). Other research has also found dissolution of quartz at 25°C, in the presence of sodium and pH of 6 (Berger et al. 1994). Hence, wind or river induced resuspension with and without saltwater electrolyte may have dissolved silica species and released silicate into the water.

The sediment organic matter, which typically consists of plankton, animal remnants, and diatoms, had a significant effect on the SiO₄ concentration in the lab experiments (Table 4.2). This may indicate that the remnants of diatoms in the sediments of both estuaries, which have been recycled into the sediment, are releasing silicate. Interestingly, only July 2012 sample from the Nueces Estuary contained one diatom species, i.e. *Navicula Sps.* In addition to recycling and releasing SiO₄ into the water, the sediment organic matter may also act as a filming effect between sediment particles and overlying water. Research has identified dissolution of biogenic silica after removing organic matter from diatom exoskeletons (Bidel and Azam 2001; Bidel et al. 2003). The filming effect of organic matter was also observed in the lab experiment. This

effect may be the reason for the reduced level of silicate in the treatments with organic matter compared to those without organic matter. The removal of organic matter might enhance the rate of reaction between sediment particles and the overlying saline water, resulting in more SiO_4 concentration in the overlying water.

The Nueces Estuary gets less freshwater inflow than the Guadalupe Estuary; however, the Nueces estuary has more organic matter than the Guadalupe Estuary. That indicates recycling induced by longer water residence times in the Nueces Estuary may have provided more organic matter than the Guadalupe Estuary. Similar silicate mineral contents in the sediments of both estuaries may be the reason why the concentration of SiO_4 was not significantly different in the two estuaries.

4.4.2. Dissolved orthophosphate in the estuary and in the lab

Phosphorus has a low bonding affinity towards water molecules compared to a high bonding affinity towards inorganic minerals, which makes phosphorus adhere to sediment particles (Bennett et al. 2001). However, agricultural and industrial activities in the watershed have increased the input of dissolved phosphate into the estuaries. In the Guadalupe Estuary, the high orthophosphate concentration in lower salinities indicates orthophosphate was getting into the estuary by freshwater inflow (Fig. 4.3). Phosphorus forms a complex with iron and aluminum ions in organic-rich freshwater sediment, which then binds to the sediment particles. When sediments interact with the more saline estuary water, phosphorus desorbs due to the decrease of iron and aluminum ions and the increase of negatively charged metal oxides (Sundareshwor and Moris 1999). The orthophosphate concentrations in the oligohaline and mesohaline regions of Guadalupe Estuary may have been caused by desorption from the sediment organic matter.

The organic sediment transported to the polyhaline regions of an estuary can flocculate and retain P-load in the sediment (Howarth et al. 1995; Nielsen et al. 2001). In the Nueces Estuary, salinity was greater than 20 ppt during most of the sampling period indicating that less freshwater inflow gets into the estuary. The higher salinity-induced flocculation may be the reason for low orthophosphate concentration in the estuary. The long term orthophosphate levels in the Nueces Estuary indicate that orthophosphate concentration may have been maintained by recycling and release from sediment organic matter, calcite-, and iron-bonded phosphate rather than freshwater inflow, except during high inflow events.

In estuaries, suspended or particulate phosphorus is bonded with organic matter, iron, aluminum, and calcite (Lebo 1991; Upchurch et al. 1974). The orthophosphate concentration in treatments with organic matter was below zero in all five samples of the 48-hr lab experiment. The added orthophosphate was not detected in the solutions with sediments collected from the Guadalupe and Nueces Estuaries. The loss of added orthophosphate may have been due to the adsorption to calcium carbonate shells (McGlathery 1994) or to iron particles (Froelich et al. 1988; Ingall and Jahnke 1997), or to the organic matter (Berner and Berner 1996). The phosphate-adsorbing sediments in the two estuaries may be adsorbing enough orthophosphate to result in lower concentrations.

Past studies have found that organic matter and iron bonded phosphorus were important in the release of phosphate into the water (Ingall and Jahnke 1997; Bianchi 2007; Krom and Berner 1981). In the lab, orthophosphate was released from the treatments without organic matter, which might be due to the oxidation of organic matter by the addition of hydrogen peroxide. Additionally, iron-bonded and calcite-bonded phosphate might be responsible for the additional

release of orthophosphate in salinity treatments without organic matter. In order to have iron-bonded phosphate release, either a high pH (i.e., close to 8) or a redox condition must be satisfied (Gomez et al. 1999). For calcite-bonded phosphate release a low pH condition is necessary (Staudinger et al. 1990; Bianchi 2007). An additional factor in the release of phosphorus from sediments was via the dissolution of calcite during sample agitation. In his experiment, Spagnoli (1999) found that phosphorus was released during resuspension from the dissolution of calcite-containing sediments. Since the present experiment was conducted at pH 7-8.5 and in the oxidizing condition, the release of orthophosphate in the treatments without organic matter is more likely due to the agitation of samples and from iron complexes. The Guadalupe Estuary sediment samples without organic treatments released more orthophosphate by the shaking procedure than the Nueces Estuary sediments (Fig. 4.6 and 4.7). The presence of more calcite in the Guadalupe Estuary sediment samples might be the reason for the higher orthophosphate level observed in the Guadalupe Estuary sediment compared to the Nueces Estuary sediment. In the treatments with organic matter, despite shaking, there was no increase in the orthophosphate concentration. The filming and adsorption effects by the organic matter present in the sediments may be the reason for the lack of increase.

4.5. Conclusions

The present study demonstrates that river inflow and sediment-water interactions are two important factors responsible for maintaining silicate and orthophosphate concentrations in the Guadalupe and Nueces Estuaries. The results of the laboratory experiments indicate sample agitation can increase in SiO_4 in fresh and saline solutions, and it is proposed that wind can play the same role in the field. Both estuaries had higher SiO_4 concentrations at higher salinities, resulting in an additional release of silicate from sediment containing silicate minerals or other silicate components, such as biogenic opal. The long-term field study identified freshwater inflow as an important source of orthophosphate for the Guadalupe and Nueces Estuaries. In the lab, added orthophosphate is adsorbed onto sediment organic matter, which explains the low concentrations found in the two estuaries. In the treatments without sediment organic matter, the orthophosphate concentration increased in the Guadalupe Estuary treatments, which contained more calcite-rich sediment compared to the Nueces Estuary treatments. The dissolution of calcite minerals, when agitated by wind forcing or river flow, may be another significant reason for the observed orthophosphate concentrations in the estuaries. Hence, this research demonstrates that interactions between physical forcing, salinity, and organic matter can regulate silicate and orthophosphate concentrations in estuaries.

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CHAPTER V

INORGANIC NITROGEN FLUXES FROM SEDIMENT AEROBIC LAYER: DOES FLUX DIFFER IN TWO DIFFERENT HYDROLOGIC FLOW REGIMES?

Abstract

The purpose of the present study was to identify fluxes of inorganic nitrogen (NH_4^+ and NO_{2+3}) in the sediment-water aerobic layer of two different hydrologic flow regimes. The watershed of the Guadalupe River/Estuary system receives more precipitation and inflow compared to the watershed of the Nueces River/Estuary system. In the field, water quality data were measured 20 cm above sediments of the Nueces River, Nueces Estuary, Guadalupe River, and Guadalupe Estuary stations during three different sampling events. Sediments samples were collected using cores, analyzed for organic matter and grain size, and also used to perform a 48 hour laboratory experiment at five different salinities. Inorganic nutrient samples were collected at five different time intervals during the experiment and samples were shaken between intervals to simulate for wind forcing. NH_4^+ concentration was higher in the Nueces River and Nueces Estuary samples as compared to similarly treated samples from the Guadalupe River and Guadalupe Estuary stations. In the estuary and river samples, NH_4^+ concentration increased with time. Disturbance of the bacterial community for the mineralization of organic matter by higher flow, and the high flow induced effect on organic matter deposition could be the reason for low NH_4^+ release in the Guadalupe River and Guadalupe Estuary treatments. An increase in NO_{2+3} concentration along salinity gradients of the Nueces Estuary treatments indicates favorable

condition for nitrification. The Guadalupe River sediments that were not exposed to salinity showed an increase in NH_4^+ concentration at 7.5 ppt salinity. This study suggests that both the hydrologic flow system and salinity have a significant effect on the retention and release of inorganic nitrogen at the sediment-water interface.

Key Words: Inorganic Nitrogen; Mineralization; Hydrologic Flow Regime; Salinity.

5.1. Introduction

Inorganic nitrogen transport to coastal waters depends on watershed landscape and inflow rates among other factors. The allochthonous organic matter transported to an estuary by river inflow may regenerate inorganic nitrogen, as Gardner et al. (2009) asserted that fresh and labile organic matter in the seasonal-hypoxic regions are important for the regeneration of nutrients.

Organic matter degradation by benthic communities facilitates nitrogen release at the sediment-water interface. The flux of inorganic nutrients from sediment to the overlying water was positively correlated with organic matter consumption by benthos (Nixon 1981; Nowicki and Nixon 1985). Redox condition (Reddy et al. 1984), sediment grain size (Nowicki and Nixon 1985), and temperature (Kemp and Boynton 1984) are the important factors that catalyzed benthic remineralization of organic matter. This degradation of organic matter is important in nitrogen cycling and maintaining estuarine productivity.

Inorganic nitrogen flux in the form of ammonium ion (NH_4^+) at the sediment-water interface enhances primary productivity of the estuary ecosystem. The released NH_4^+ is oxidized to nitrate (NO_3^-), which is a dissolved and biologically available form of nitrogen. Texas estuaries are nitrogen-limited (Gardner et al. 2006; Brock 2001), and arid coastal South Texas estuaries are deprived of significant surface inflow driven nutrient inputs (Paudel and Montagna 2014). However, these estuaries have a discernible levels of ammonia regeneration (Gardner et al. 2006). High levels of ammonia regeneration could be due to an ion pairing effect (Gardner et al. 1991; Giblin et al. 2010) and sea water cation effect (Seitzinger et al. 1991) under a constant high level of salinity. The flux of ammonia and nitrite+nitrate (DIN) in Texas estuaries depends on nitrification, denitrification, and dissimilatory nitrate reduction to ammonia (DNRA) (Twilley

et al. 1999; Yoon and Berner 1992; Gardner et al. 2006). In addition to different processes it is important to identify fluxes of DIN in the sediment-water aerobic layer of shallow Texas estuaries that experience frequent wind-driven mixing effects. Furthermore, the study of DIN fluxes by two different types of sediments in two different hydrologic systems is important for the sustainable management of aquatic ecosystems.

The main purpose of the present study was to identify fluxes of inorganic nitrogen in the aerobic layers at the sediment-water interface using sediments from two different hydrologic systems. Annual freshwater inflow to the Guadalupe Estuary is almost eight times higher than the Nueces Estuary (Montagna et al. 2013). The Nueces Estuary is a heterotrophic net ecosystem metabolism (NEM) system while the Guadalupe Estuary is a more autotrophic NEM system (Russell and Montagna 2007). The end result is that organic loading may be higher in the Nueces Estuary than the Guadalupe Estuary. Russell and Montagna (2007) determined that a decrease in salinity in the Nueces Estuary could increase organic loading. The higher inflow induced a lower C:N ratio at station B of Guadalupe Estuary (Russell and Montagna 2007). Furthermore, the high inflow could potentially wash away the planktonic community and labile organic matter, and thus, may result in a lesser regeneration of inorganic nitrogen. Nixon (1981) pointed out that surface inflow induced anthropogenic nitrogen input can overwhelm remineralization released of nitrogen to the overlying water. However, the lack of nitrogen transport from the watershed because of curtailed inflow could promote recycling and remineralization resulting in higher nitrogen fluxes in the low flow system.

Furthermore, Nixon (1981) also pointed out that the seasonal changes between inorganic and organic forms of nutrients in the coastal and marine systems occurred by rapid uptake and rapid

regeneration (in hours and days). Low inflow and high residence time in the Nueces Estuary might allow for accumulation of more organic nitrogen; thus, it might promote rapid regeneration resulting in rapid shifts into different forms of nitrogen. Hence the major question asked in the present study was: (1) Does ammonia and nitrite+nitrate flux at the sediment-water interface vary in two different hydrologic systems? A 48-hour long laboratory experiment to identify inorganic nitrogen was conducted to determine nutrient adsorption or release in the sediment aerobic layer to/from sediments during resuspension.

5.2. Study Sites and Method

Sediment and water samples were collected from two different watersheds in South Texas, USA. In the Guadalupe River/Estuary system, sediment and water samples were collected from the Guadalupe River and from the Guadalupe Estuary proper, but close to the river mouth (Fig. 5.1). The river water samples were collected from a station downstream of the confluence point between the San Antonio and Guadalupe Rivers (Fig. 5.1). Similarly, in the Nueces River/Estuary system, sediment and water samples were collected from the Nueces River, and from the Nueces Estuary proper, but close to the river mouth. The river water samples were collected at a station within LaBonte Park below the Calallen Dam at the confluence point between the ephemeral Hondo Creek and the Nueces River (Fig. 5.1). In the case of both watersheds, the river sampling stations were close to the USGS gaging and water quality stations (USGS station ID 08188810 was close to the Guadalupe River station, whereas USGS station ID 08211500 was close to the Nueces River station).

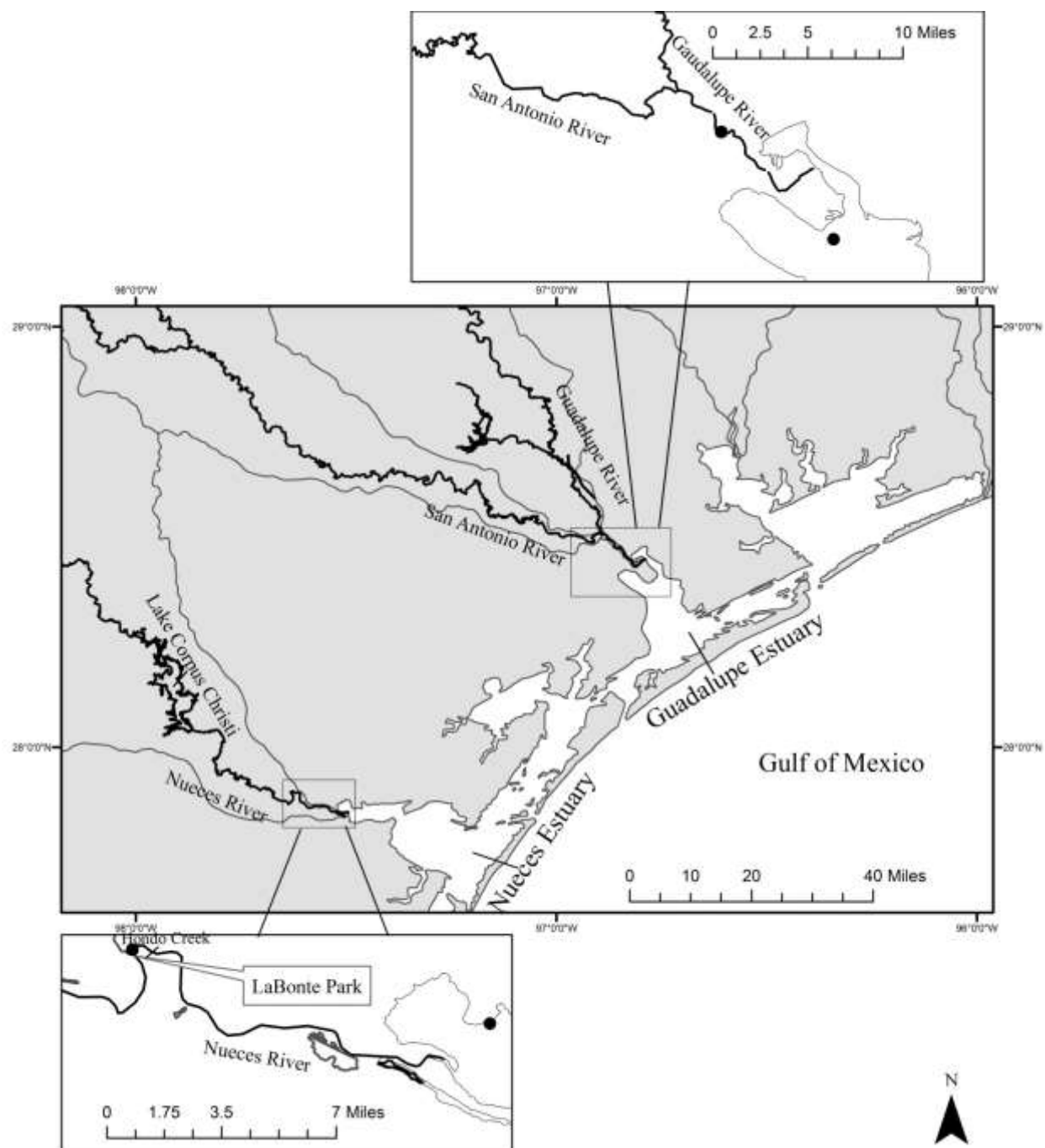


Fig. 5.1 Map of Study Sites with sampling stations.

At all sampling stations, water column dissolved oxygen, pH, temperature, salinity, total suspended solids (TSS), chlorophyll-a, and inorganic nutrients [ammonia (NH_4^+), nitrite+nitrate (NO_{2+3}), orthophosphate (o-PO_4), and silicate (SiO_4)] were measured close to the bottom sediments. A YSI Hydro Sonde was used to measure DO, pH, temperature and salinity. TSS was measured by filtering a known volume of water and drying in the oven. Chlorophyll-a was measured using a non-acidic method (Krauk et al. 2006). Inorganic nutrients were measured by using an O.I.A. segmented flow autoanalyzer. In Table 5.1, water quality and sediment characteristics from the four sediment collection sites for our laboratory experiments were tabulated.

5.2.1. Sediment sample collection sites

The top 3 cm of sediments were collected using cores from the river mouth of two estuaries during July 2012, October 2012, and January 2013 quarterly samplings and from the rivers during June 2013, Oct 2013, and February 2014. In the field, sediment samples were kept on ice and stored frozen upon transfer to the lab in order to slow organic matter degradation. Organic matter contents, grain size analysis, and inorganic nitrogen flux experiments were performed by using these sediment samples. Sediments were air dried for 24 hours before using for the laboratory experiment to facilitate weighing and handling.

5.2.2. Grain size analysis

Grain size was analyzed using a Beckman Coulter LS 13 320 Laser Particle Size Analyzer. Sediment samples were homogenized, placed into centrifuge tubes, and the organic matter removed by hydrogen peroxide digestion. Digested samples were washed three times with

deionized water, and wet sieved using 2 mm size sieve to remove any grains coarser than sand. Then the samples were centrifuged at 5000 RPMs for 5 minutes to settle all the fine particles. As the sediment samples were size/density graded following centrifugation, they were manually homogenized into slurry in the centrifuge tube to ensure that extracted subsamples would have a representative grain size distribution. Subsample scoops were extracted from the slurry for analysis with the laser particle size analyzer. The instrument and associated software provide grain size distribution results in 92 size fractions ranging from 0.4 to 2000 μm as both volume and surface area percentages. In this study, particle size diameters of 0.4 – 4 μm were considered as clay, 4 – 63 μm as silt, and greater than 63 μm as sand particles.

5.2.3. Organic matter

The organic matter content in the sediment samples was determined by mass loss following overnight combustion of samples at 385 °C (Schumacher 2002). Sediment samples were first weighed and then combusted. Then the samples were cooled in a desiccator and reweighed. The difference between initial and final weights gives organic matter content in the sample.

5.2.4. Laboratory experiments

The laboratory experiment was conducted at room temperature. The sediment was carefully homogenized before using for the analysis.

5.2.4.1. Preparation of nutrients spike solution

Primary standards with concentrations of 10,000 $\mu\text{mol/L}$ were prepared using 0.851 g of undry potassium nitrite, 1.011 g of dry potassium nitrate, and 0.661 g of dry ammonium sulfate. Each chemical was weighed out, placed in a 1000 ml volumetric flask, dissolved and brought up to 1000 ml with freshly drawn Milli-Q deionized water. From these refrigerated primary standards, a 100 ml mixed stock standard was prepared daily containing 250 $\mu\text{mol/L}$ of nitrite, 250 $\mu\text{mol/L}$ of nitrate and 500 $\mu\text{mol/L}$ of ammonia. That solution was then used to ‘spike’ the samples with additional nutrients in the following experiments.

5.2.4.2. Experimental design for laboratory study

All the laboratory experiments to identify sediment nitrogen flux were performed within two weeks of sample collection. The laboratory experiment was conducted using sediments with organic matter at five different salinity solutions over a period of 48 hours. The five salinity solutions of 0 (DI water), 7.5, 15, 25, and 35 ppt were prepared using low nutrient sea water (LNSW) and DI water. The inorganic nitrogen flux was measured at five different intervals after the addition of sediment. During each experiment the sediment to salinity solution ratio was prepared in a 1:30 ratio by mixing 4 g of sediment and 120 ml of solution in a 250 ml polycarbonate Erlenmeyer flask. The experiment was conducted with two replicates for each salinity solutions by using rivers and estuaries sediments. Each flask was supplemented with the spike nutrient solution to provide an additional concentration 5 $\mu\text{mol/L}$ of NH_4^+ , 2.5 $\mu\text{mol/L}$ of nitrite (NO_2) and 2.5 $\mu\text{mol/L}$ of nitrate (NO_3).

The spiked salinity solutions, with the added inorganic nitrogen concentration, were carefully mixed prior to adding the weighed sediment to each flask. After sediment addition, a 3-5 ml

sample was collected from each flask, using a large bore plastic syringe, to be used as the baseline measurement (T_1). Additional water samples for nutrient analysis were then collected at 10 minutes (T_2), 50 minutes (T_3), 360 (T_4) minutes and 48 hours (T_5) after the addition of sediment to the flasks. The flasks were shaken vigorously using an oscillating shaker between each sampling time. The samples were shaken for approximately 50 seconds at the following intervals: every 2 minutes between T_1 to T_2 , every 5 minutes between T_2 to T_3 , every 15 minutes between T_3 to T_4 and every hour between T_4 to T_5 . The samples were allowed to settle for 10 hours overnight and the agitation protocol was resumed the following day.

A control was prepared using the nutrient spike solution at the same salinity, and nutrient concentration as in the experimental flasks but without the sediment addition. The control was designed to identify and measure the degradation of nutrients in the solutions over the time of experiment without sediment influence. The obtained NH_4^+ and NO_{2+3} concentrations were the concentrations after subtracting the control sample's concentrations at that given time. Hence, the negative and positive values indicate adsorbed and released concentrations to and from the sediments.

5.2.4.3. Inorganic nutrients analyses

A 3-5 ml sample for nutrient analysis was extracted from each polycarbonate Erlenmeyer flask using a syringe and filtered through nuclepore polycarbonate 0.45 μm membrane filter paper. Each sample was kept frozen in a labeled vial until analysis. An O.I.A. segmented flow autoanalyzer was used for the nutrient analysis. A concentration of 0.25 $\mu\text{mol/L}$ was the lower detection limit of NH_4^+ and NO_{2+3} used while preparing the standard curve. The O.I. Segmented flow autoanalyzer manufacturer recommended method detection limit (MDL) range is 0.1-10

$\mu\text{mol/L}$ for NH_4^+ and 0.02-40 $\mu\text{mol/L}$ for NO_{2+3} . The concentrations higher than the MDL range were identified by sample dilution. The concentrations less than the MDL were not considered during the analysis.

In the O.I.A. flow autoanalyzer, the sample NH_4^+ ion reacts with alkaline phenol and hypochlorite to form indophenol blue that is proportional to ammonia concentration. The obtained blue color was intensified with sodium nitroferricyanide and absorbance was measured at 640 nm. For the analysis of NO_{2+3} , nitrate was reduced quantitatively to nitrite by cadmium metal. The formed nitrite plus the sample nitrite (i.e. originally present in the sample) was diazotized with sulfanilamide and subsequently coupled with N-(1-naphthyl) ethylenediamine dihydrochloride. The obtained highly colored azo dye was colorimetrically detected at 540 nm. Thus, the final concentration would be nitrite+nitrate (i.e. NO_{2+3})

5.2.5. Analytical Method

The data set was analyzed using the SAS 9.3 statistical software package. PROC GLM was used to perform analysis of variance (ANOVA), PROC SGSCATTER was used to obtain NH_4^+ and NO_{2+3} concentrations along salinity gradients, and PROC GCHART was used to show NH_4^+ and NO_{2+3} concentrations over the time of experiments.

5.3. Result

5.3.1. Field physicochemical parameters

The average salinity was higher in the Nueces Estuary than other three study sites (i.e. the Nueces River, and the Guadalupe River and Estuary stations). Salinity at the Nueces River station was higher and comparable with the Guadalupe Estuary. NO_{2+3} was significantly higher in the Guadalupe River; the three months average NO_{2+3} concentration was more than 100 $\mu\text{mol/L}$ in the Guadalupe River, whereas, except in the January month when NO_{2+3} was 18.2 in Guadalupe Estuary, NO_{2+3} concentration in both estuaries was less than 0.5 $\mu\text{mol/L}$. The NO_{2+3} concentration in the Nueces River and Nueces Estuary were almost similar. NH_4^+ was higher in the two river sites compared to their respective estuary stations, except in October when the Nueces Estuary (0.78 $\mu\text{mol/L}$) NH_4^+ was higher than the Nueces River (0.28 $\mu\text{mol/L}$). Silicate and orthophosphate concentrations were higher in the river sites compared to their respective estuaries in all samples. TSS values in the Guadalupe River were significantly higher than the Guadalupe Estuary. TSS values in the Nueces Estuary were higher than the Nueces River in October and January. In the Nueces River and Nueces Estuary, chlorophyll-a constituted a significantly large portion of TSS (Table 5.1). The chlorophyll-a was comparable among the Guadalupe Estuary, Nueces Estuary, and Nueces River stations, whereas the Guadalupe River station chlorophyll-a was the lowest (Table 5.1).

Table 5.1 Water quality parameters and sediment characteristics in the Guadalupe Estuary (GE-estuary), Nueces Estuary (NC-estuary), Guadalupe River (GE-river) and Nueces River (NC-river)

Sites	Months	Salinity (ppt)	Temperature (°C)	pH	DO (mg/L)	NO ₂₊₃ (μmol/L)	NH ₄ ⁺ (μmol/L)	o-PO ₄ (μmol/L)	SiO ₄ (μmol/L)	TSS (mg/L)	Chl-a (μg/L)	Organic content (%)	Sand (%)	Silt (%)	Clay (%)
GE-estuary	July	9	28.61	8.29	6.16	<0.25	0.75	2.59	161.69	33.5	19.63	2.7106	23.6	54.9	21.5
	Oct	15.6	24.08	8.44	9.15	0.35	2.13	3.3	222.47	31.12	26.77	4.6487	39.6	44.1	16.3
	Jan	24.36	14.3	8.46	13.07	18.2	0.68	1.06	36.17	22.43	14.73	2.3290	22.0	45.9	32.1
NC-estuary	July	31.96	29.58	8.06	5.5	0.46	0.92	1.98	136.78	22.66	6.7	3.3888	60.0	26.6	13.4
	Oct	42.02	25.23	8.03	7.75	<0.25	0.78	1.81	121.42	26.8	26.23	3.9940	39.2	38.5	22.3
	Jan	40.15	11.49	8.11	10.07	3.38	2.19	1.47	68.51	47.5	17.86	2.6305	17.0	35.3	47.7
GE-river	June	0.23	30.41	8.32	5.48	98.97	4.2	6.38	243.87	83.04	6.78	3.2561	12.3	49.2	38.5
	Oct	0.16	23.5	8.39	9.86	150.7	2.14	8.9	194.6	84.87	1.41	2.1237	10.6	53.9	35.5
	Feb	0.41	13.16	8.61	9.72	164.1	2.4	12.7	55.5	46.05	9.85	2.0376	7.5	54.8	37.7
NC-river	July	3.3	28.3	8.5	-----	0.61	3.27	8.2	368.2	27.2	16.97	3.3555	33.1	49.0	17.9
	Oct	16.74	25.3	8.2	7.61	1.76	0.28	12.54	394.22	17.74	20.3	3.7739	40.2	42.3	17.5
	Feb	6.5	13.32	8.04	9.91	1.71	1.81	3.09	238.6	23.13	50.2	2.7551	51.9	28.7	19.4

Table 5.2 ANOVA result to show the NH₄ and NO₂₊₃ concentration difference in the studied estuaries and rivers treatments. The p-value with * indicates significant value.

Dependent	p-value				
Variable	Estuaries	Time	Salinity	Salinity*Estuaries	Salinity*Time
NH ₄ ⁺	0.03*	<0.0001*	0.0038*	0.9795	0.9943
NO ₂₊₃	0.14	0.1334	0.8672	0.0337*	0.1083
	Rivers	Time	Salinity	Salinity*Rivers	Salinity*Time
NH ₄ ⁺	<0.0001*	<0.0001*	0.0395*	<0.0001*	0.0007*
NO ₂₊₃	0.383	0.66	0.652	0.5908	0.4156

5.3.2. Flux of NH_4^+ and NO_{2+3} from estuaries sediments

NH_4^+ concentration increased from time- T_1 to time- T_5 in both estuary treatments; however, the increase was more from time- T_4 to time- T_5 in all the Nueces Estuary treatments [i.e. in DI treatment NH_4^+ increased from 8.58 to 26.69 $\mu\text{mol/L}$, and in all salinity treatments from 4.50 to 18.22 $\mu\text{mol/L}$]. The highest NH_4^+ concentration was 26.69 $\mu\text{mol/L}$ in the Nueces Estuary DI treatment at time- T_5 . In the Guadalupe Estuary, NH_4^+ concentrations in DI treatments from time- T_2 to time- T_5 were almost similar. The highest NH_4^+ concentration in the DI treatment of the Guadalupe Estuary was 10.8 $\mu\text{mol/L}$ at time- T_4 (Fig. 5.2). NH_4^+ concentration was significantly different between estuaries, salinity, and time (Table 5.2).

NO_{2+3} did not increase from initial concentration at time- T_1 to time- T_5 in the Guadalupe Estuary DI treatment. With the exception of the Guadalupe Estuary DI treatment, in all treatments (i.e. all treatments of the Nueces Estuary and saline treatments of the Guadalupe Estuary) NO_{2+3} increased from time- T_1 to time- T_5 . The NO_{2+3} concentrations were higher in the Guadalupe Estuary versus the Nueces Estuary DI, salinity-7.5, and salinity-15 treatments. In comparison, the Nueces Estuary salinity-25 and salinity-35 treatments had more NO_{2+3} than the Guadalupe Estuary salinity-25 and salinity-35 treatments (Fig. 5.2). NO_{2+3} concentration was not significantly different between estuaries, salinity, and time. NO_{2+3} was significantly different with the interaction between estuaries and salinity (Table 5.2).

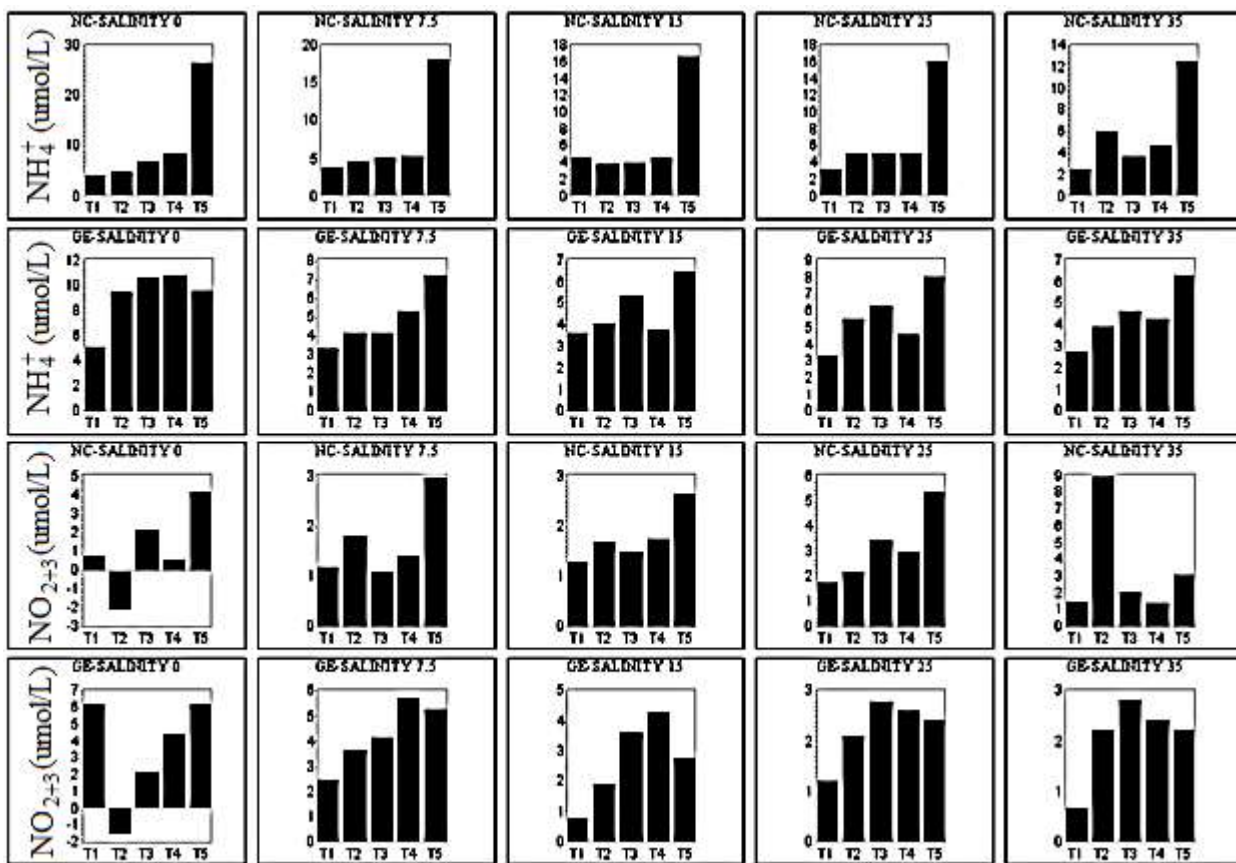


Fig. 5.2 Average ammonia and nitrite+nitrate flux in sediment-water aerobic layers of the Guadalupe and Nueces Estuaries treatments.

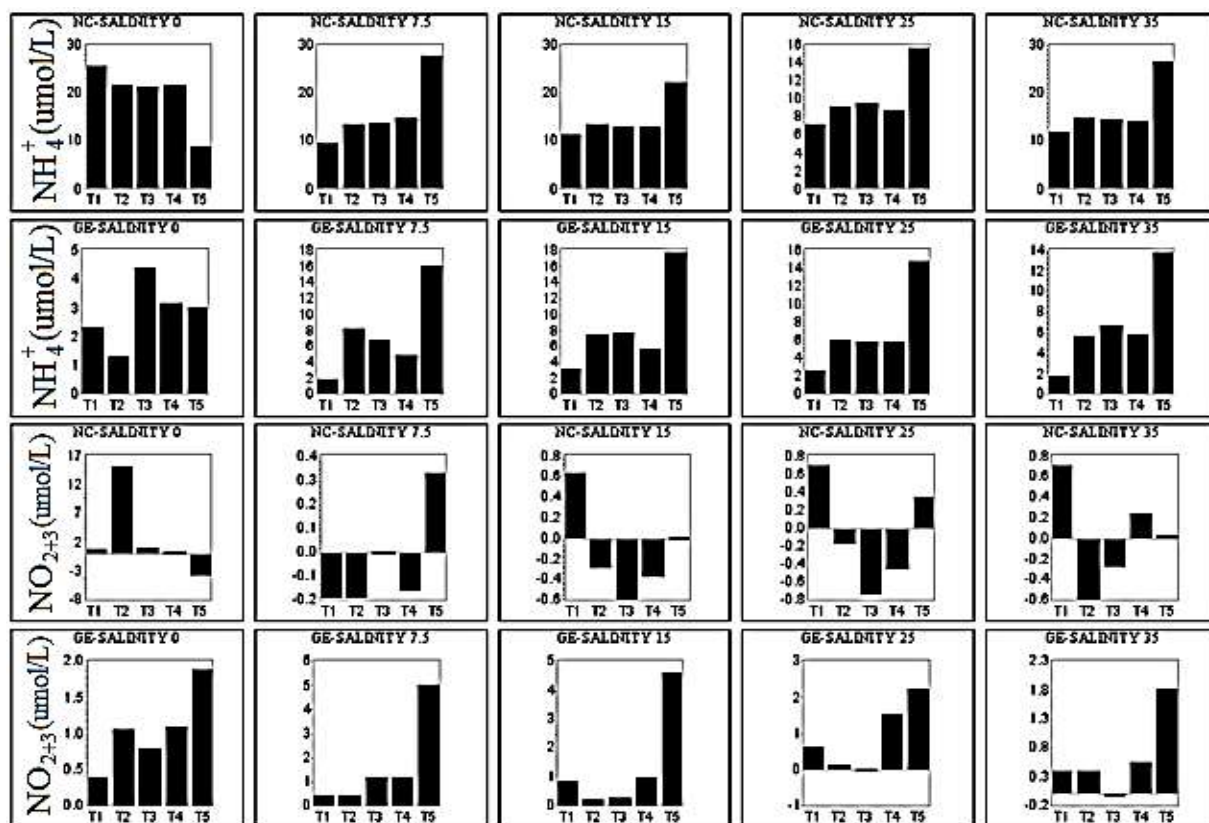


Fig. 5.3 Average ammonia and nitrite+nitrate flux in sediment-water aerobic layers of the Guadalupe and Nueces Rivers treatments.

5.3.3. Flux of NH_4^+ and NO_{2+3} from river sediments

Except in salinity-25 treatment, the final NH_4^+ concentrations at time- T_5 were greater in the Nueces River treatment than in the Guadalupe Estuary treatment. In the Nueces River and Guadalupe River salinity treatments NH_4^+ concentration increased from time- T_1 to time- T_5 . However, in the DI treatment of the Nueces River, NH_4^+ concentration at time- T_5 was 16.7 $\mu\text{mol/L}$ less than at time- T_1 . Most of the identified NH_4^+ concentrations in the salinity treatments were greater at that given time in the Nueces River compared to the Guadalupe River (Fig. 5.3). NH_4^+ concentration was significantly different between rivers, salinities, and time (Table 5.2).

In contrast to NH_4^+ , NO_{2+3} concentration at time- T_5 in all saline treatments were greater in the Guadalupe River treatments than in the Nueces River treatments. The Nueces River saline treatments showed very low levels of NO_{2+3} . In most of the Nueces River saline treatments the measured NO_{2+3} concentrations in the solution were less than the added 5 $\mu\text{mol/L}$ (Fig. 5.3). NO_{2+3} concentration was not significantly different between rivers, salinities, and time (Table 5.2).

5.3.4. NH_4^+ and NO_{2+3} along salinity gradient

NH_4^+ concentration in the solution decreased along salinity gradients in the Guadalupe Estuary and the Nueces Estuary treatments. In both estuaries treatments, sharp decrease was observed from 0 to 7.5 ppt. NO_{2+3} in the Nueces Estuary treatments was continuously increasing from 0 to 35 ppt, whereas NO_{2+3} in the Guadalupe Estuary treatments increased from 0 to 7.5 and then decreased to 35 ppt (Fig. 5.4).

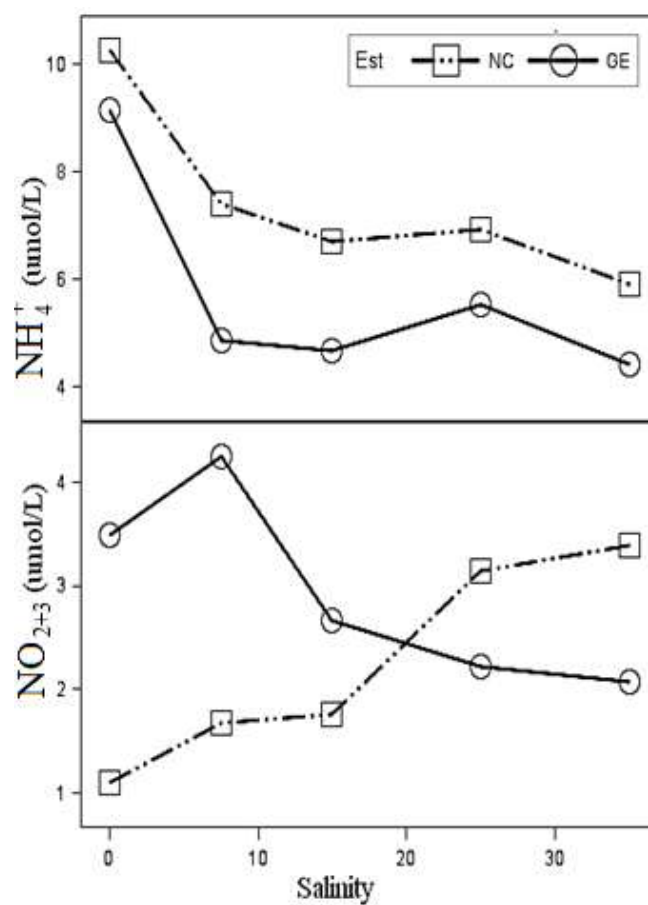


Fig. 5.4 Average NH_4^+ and NO_{2+3} retained and released to and from aerobic layers of estuaries sediment along salinity gradients. Depicted concentration was obtained after subtracting control value. Each point was the average concentration at five different times.

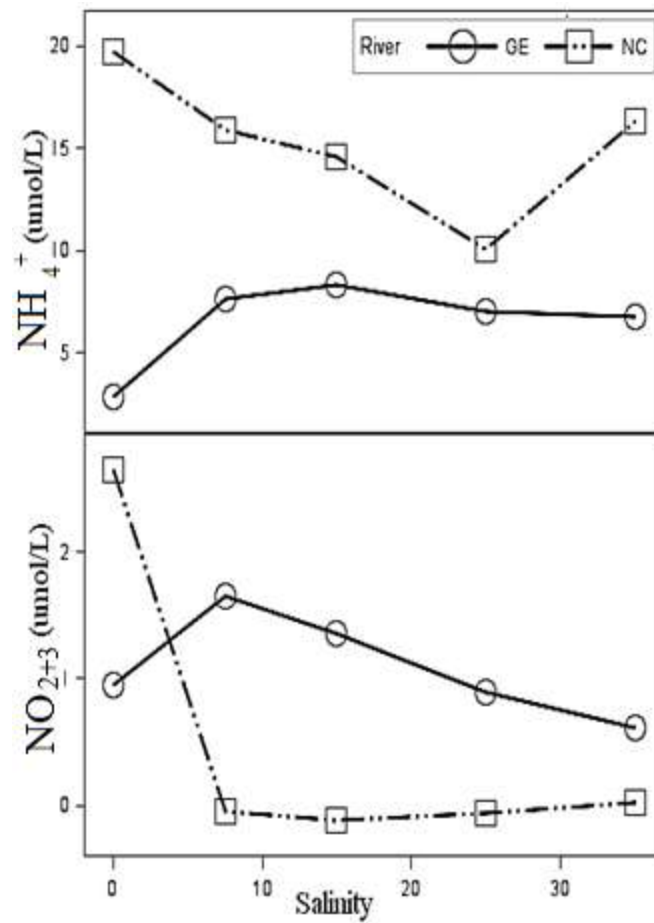


Fig. 5.5 Average NH_4^+ and NO_{2+3} retained and released to and from aerobic layer of river sediment along salinity gradients. Depicted concentration was obtained after subtracting control value. Each point was the average concentration at five different times.

NH_4^+ concentration in the Nueces River treatments decreased from 0 to 25 ppt and then increased from 25 to 35 ppt. In the Guadalupe River treatments, NH_4^+ concentration increased from 0 to 7.5 ppt and then remained approximately constant from 7.5 to 35 ppt. In the Nueces River treatments, NO_{2+3} decreased sharply from 0 to 7.5 ppt, and then concentrations were less than the added 5 $\mu\text{mol/L}$ throughout 35 ppt. In the Guadalupe River treatments, NO_{2+3} concentration increased from 0 to 7.5 ppt, and then decreased slowly from 7.5 to 35 ppt (Fig. 5.5).

5.3.5. Sediment organic matter and grain size

In the Guadalupe Estuary, Nueces Estuary, and Nueces River sediments, organic matter content was high in October. The three months average organic matter in the Guadalupe Estuary, Nueces Estuary, Guadalupe River, and Nueces River were 3.23%, 3.33%, 2.47%, and 3.29% respectively. The Nueces Estuary sediment had a high percentage of coarser particles (i.e. 60% sand) in July while high percentage of finer particles (i.e. 83% silt+clay particles) in January. The Guadalupe Estuary sediment had high coarser particles (i.e. 39.6% sand) in October while a high percentage of finer particles (i.e. 78.0% silt+clay) in January. The three months average sediment grain size identified coarser particles in the Nueces River sediments (41.7% sand) than in the Guadalupe River sediments (10.1% sand) (Table 5.1). The surface area of coarser particles dominated sediments from the Nueces Estuary and Nueces River showed similarity with the relatively finer sediments from the Guadalupe Estuary and Guadalupe River (Fig. 5.6). In sediments from all four locations, approximately 80% of the surface area was attributed to particles in the clay size range (i.e. particle diameter from 0.4 – 4 μm , see Fig. 5.6).

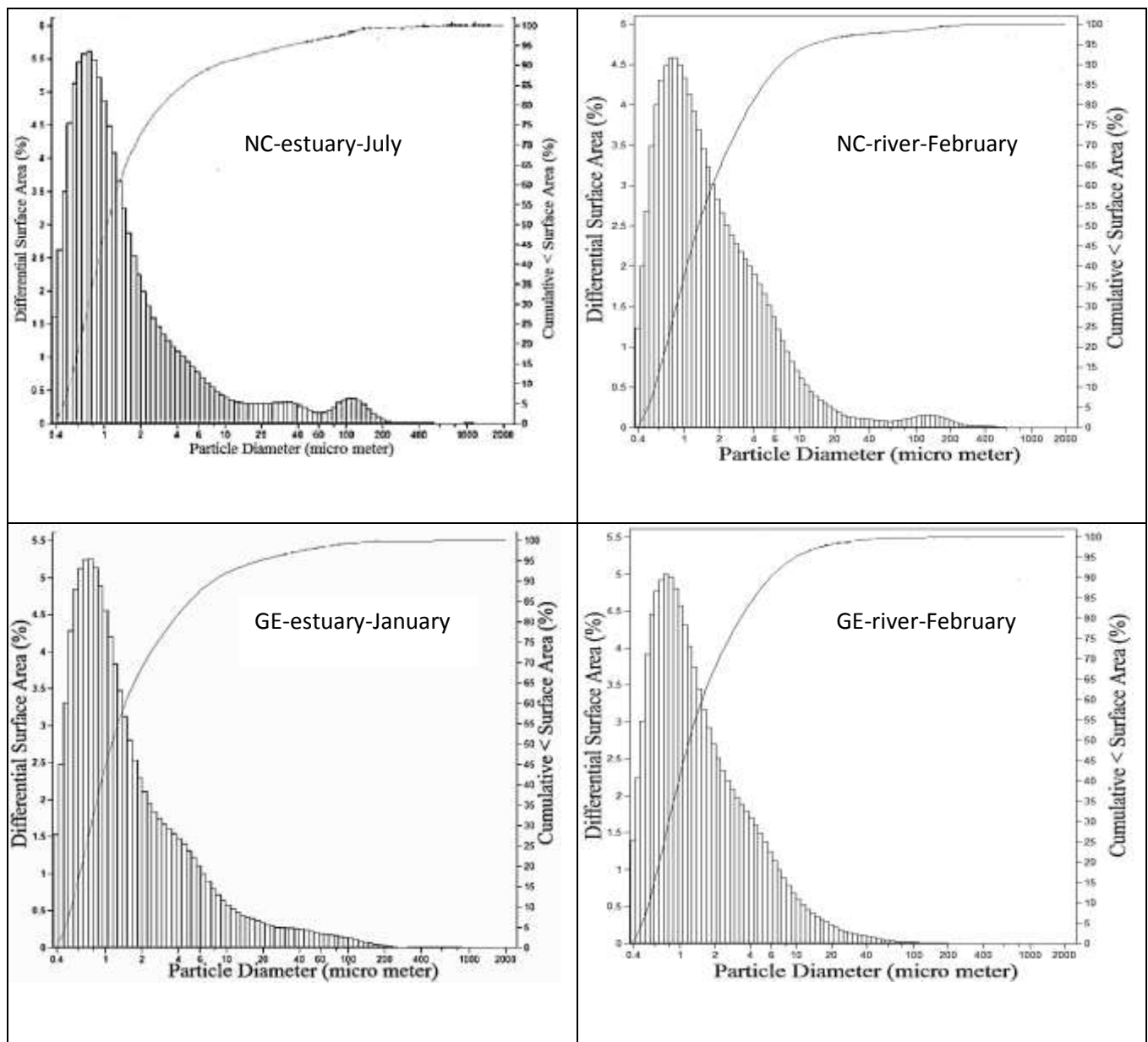


Fig. 5.6 Variation in surface area with respect to sediment particle diameter. Top two from the Nueces Estuary and Nueces River were examples of sediment surface area dominated by coarser particles. Bottom two from the Guadalupe Estuary and Guadalupe River were examples of sediment surface area dominated finer particles.

5.4. Discussion

Nitrate is the dissolved form of inorganic nitrogen (Stanley, 2002), and freshwater inflow transports it from a watershed to an estuary. The high NO_{2+3} concentration ($>100 \mu\text{mol/L}$) in the Guadalupe River sample indicates river inflow was a major source of NO_{2+3} to the Guadalupe Estuary (Table 5.1). The USGS gaging station flow data on the Nueces River (USGS Station ID 08211500) and Guadalupe River (USGS station ID 08188810) showed low flow in the Nueces River compared to the Guadalupe River. Most of the time the Nueces River showed a base flow condition, which could be the reason for low NO_{2+3} concentrations in the Nueces River and Nueces Estuary treatments. In the Nueces Estuary and Nueces River, the N (i.e. $\text{NH}_4^+ + \text{NO}_{2+3}$) : P (i.e. o-PO_4) ratio was below the red field 16:1 ratio, whereas in the Guadalupe River it was above 16:1. In the Guadalupe Estuary, the N:P ratio was higher than 16:1 for the January sample (Table 5.1). This indicates the Nueces Estuary and Nueces River were N-limited.

In the Nueces Estuary, salinity was higher than 30 ppt not only during the three sampling events for the present study, but also during the April 2011 to October 2013 samplings. Salinity at the Nueces River station at LaBonte Park was comparable with the salinity of the Guadalupe Estuary, and this is likely due to inflow from Hondo Creek. Generally, the Nueces River water does not overtop the Calallen Dam, hence, evaporation could have led to the accumulation of salt. However, Hondo Creek enters the Nueces River below Calallen Dam, drains agricultural and wetland areas, and is known to be a small source of freshwater to the river (BOR 2000).

TSS concentration was higher in the Guadalupe River stations compared to the other three stations, and this indicates more flow in the river. Chlorophyll-a was identified to be low at the turbidity maximum (Herman and Heip 1999), which was observed in the Guadalupe River during high TSS concentration (Table 5.1). Even though inflow driven inorganic N and N:P

ratios were low in the Nueces River and Nueces Estuary, chlorophyll-a was comparable with the Guadalupe Estuary. The high chlorophyll-a concentration might be due to the flux of N from sediment mineralization.

5.4.1. Sediment-water NH_4^+ fluxes over the time

The idea of using a homogenized, upper 3 cm sediment sample, and performing an experiment with the aerobic sediment layer was useful in recognizing the sediment aerobic layer nitrogen release from two different systems. Ammonium exchange between sediment aerobic and anaerobic layers depends on different factors such as the concentration gradient between the two layers, the different types of cations involved, the regeneration rate of N in anaerobic layers, the cation exchange capacity of soil, the diffusion rate in sediment layers, and soil porosity (Reddy et al. 1984). The use of the sediment aerobic layer in the present study would eliminate the effect of different processes that take part in altering ammonium ions in the sediment system. The change in concentration would therefore be strictly determined by the sediment aerobic layer.

Salinity and NEM were negatively correlated in the study of Lavaca and Nueces Bays (Russell and Montagna 2007). Station NC-B studied by Russell and Montagna (2007) was close to our station in the Nueces Estuary for the present study. The inverse relationship between NEM and salinity indicates the system functions as a heterotrophic NEM system as salinity increases. Furthermore, Russell and Montagna (2007) emphasized that the decrease in salinity due to fresh water inflows would increase organic loading in the Nueces Estuary, whereas the same decrease in salinity would increase nutrient loading in the Guadalupe Estuary. Therefore, organic matter could reach higher concentrations in the Nueces Estuary compared to the Guadalupe Estuary.

The high level of ammonia concentration in the Nueces Estuary treatments over the time of the experiment supports the presence of organic matter in the sample (Fig. 5.2). Ammonification, in which NH_4^+ is produced by the bacterial decomposition of organic matter, breaks down organic nitrogen in the water column and sediment (Bianchi 2007). The release of NH_4^+ over the duration of experiment indicates N mineralization. Although the Guadalupe Estuary treatments did show NH_4^+ release comparable to the Nueces Estuary treatments until time-T4, the significant difference in release between time-T4 and time-T5 in those two estuary treatments indicate the Nueces Estuary sediments had more organic matter, or had more sediment particles bonded with NH_4^+ ions, than in the Guadalupe Estuary. Interestingly though, the average sediment organic matter in our three sediment samplings in the Nueces Estuary was 3.33 mg/gm, which is higher than the 3.23 mg/gm found in the Guadalupe Estuary sediment. NH_4^+ flux was high during base flow conditions in Copano Bay, Texas (Bruesewitz et al. 2013). This is possible if there is more organic matter and favorable conditions for N mineralization in the sediments from Nueces Estuary, which experiences base flow conditions most of the time, compared to the Guadalupe Estuary sediments where there is higher flow. Thus, this could be the reason for more NH_4^+ concentration in all of the Nueces Estuary treatments versus the Guadalupe Estuary treatments. NH_4^+ regeneration was reported to be around $0.2 \mu\text{molL}^{-1}\text{h}^{-1}$ in Texas estuaries (Gardner et al. 2006). The NH_4^+ release in all treatments of the Guadalupe and Nueces Estuaries supports regeneration in Texas estuaries reported by Gardner et al. (2006). High FWI in the Guadalupe Estuary as compared to the negligible flow in the Nueces Estuary might have a detrimental effect on the accumulation of the sediment organic load. Furthermore, the inflow pressure in the Guadalupe Estuary would likely wash away labile and stable organic matter so that bacterial mineralization might be hindered. Also, inflow pressure could have simply stressed

the microbial community. The experiment results of NH_4^+ release over the 48 hour period supports the hypothesis of low stability due to the inflow effect on the Guadalupe Estuary sediment organic matter, and could explain the reduction in NH_4^+ release in the Guadalupe Estuary treatments.

5.4.2. Sediment-water NH_4^+ flux and salinity effect

The nature of NH_4^+ release over the time duration of the experiment with the Nueces River treatments was similar to that of the Nueces Estuary treatments except for a higher magnitude of NH_4^+ released from the Nueces River treatment. Differences in NH_4^+ release between time- T_4 and time- T_5 were higher in the Guadalupe River treatments than for the same time range in the Guadalupe Estuary treatments (Figs. 5.2 and 5.3). The Guadalupe River never had salinity higher than 0.41 ppt (Table 5.1) during any of our sampling events. When freshwater sediments come in contact with saline water, NH_4^+ ions have to compete for adsorption sites with salt water cations, which results in free NH_4^+ in solution (Gardner et al. 1991). Thus, the ion pairing effect described by Gardner et al. (1991) could be the reason for higher NH_4^+ released by the Guadalupe River sediments versus the Guadalupe Estuary sediments. The lower release in the Guadalupe River DI treatments compared to the Guadalupe River salinity treatments also indicate a salinity effect on the experimental NH_4^+ release from the Guadalupe River sediments. Seitzinger et al. (1991) identified river and estuary sediments incubated with freshwater had more exchangeable NH_4^+ than sediments incubated with saltwater. In the current study NH_4^+ concentrations in the DI treatments of Nueces Estuary, Nueces River, and Guadalupe Estuary were the highest, and the concentration decreased along the salinity gradients (Figs. 5.4 and 5.5). The three treatments, which showed high NH_4^+ concentration in the DI treatments, were always

in contact with salt water, whereas the Guadalupe River sediments very rarely come in contact with salt water. Sediments that come in contact with salt water could dissociate NH_4^+ ions from sediment negatively charged particles due to the salt water effect and ion pairing effect (Seitzinger et al. 1991; Gardner et al. 1991). The increases in NH_4^+ in the 7.5 ppt salinity treatments as compared to the DI treatments (see Fig. 5.5) of the Guadalupe River sediments indicates the ion pairing effect discussed by Gardner et al. (1991). The three salinity treatments of the Guadalupe River showed similar NH_4^+ concentration to those of the 7.5 ppt salinity treatments, and this could be due to the lack of NH_4^+ supply in the reddish brown Guadalupe River sediments.

For sediment that has already come in contact with salt water and then diluted with freshwater, the NH_4^+ ion present in the pore water might diffuse into the freshwater in the form of NH_4OH and NH_4^+A^- . This might be the reason for the higher detectable NH_4^+ concentration in our DI treatments of the Nueces Estuary, Nueces River, and Guadalupe Estuary sediments versus the salinity treatments from the same. Bernard et al. (2007) concluded that intermediate salinity (i.e. 5 and 10 ppt) favors nitrification, and thus, high nitrification rates. The lower NH_4^+ concentration resulting from the salinity treatments compared to the DI treatments of the Nueces Estuary, Guadalupe Estuary, and Nueces River indicates that nitrification may be occurring in the salinity treatments. The gradual increase in NO_{2+3} concentration along salinity gradients in the Nueces Estuary treatments could be due to nitrification by the surplus bacterial community. In addition to the favorable environment for nitrification in the salinity treatments, volatilization loss of NH_4^+ might have also possibly occurred in the salinity treatments of the Nueces Estuary, Nueces River, and Guadalupe Estuary sediments. Volatilization loss of NH_3 in flooded soil depends on pH and temperature. It has been recognized at $\text{pH} \geq 7.5$, and is a serious concern

when $\text{pH} > 8$ (Reddy et al. 1984). In this study, the pH values of the 25 and 35 ppt salinity treatments were greater than 8. Thus, the decrease in NH_4^+ concentration in the salinity gradient of most of the treatments could be possible due to the volatilization loss of NH_3 .

The findings of the present study indicate that when freshwater sediment is mixed with saline estuary water, NH_4^+ ions might be released into the water column and sediment aerobic layer. However, sediment that has already been in contact with salt water might not release NH_4^+ unless the salt concentration exceeds the preexisting pore water concentration.

5.4.3. Sediment composition and ammonia flux

The sediments from the Nueces Estuary were coarser than the Guadalupe Estuary sediments, whereas they had nearly identical amount of organic matter (Table 5.1). The grain size distribution of sediment is directly related to the amount of surface area available to adsorb pollutants and cations. Particles finer than $63\ \mu\text{m}$ in diameter (i.e. clays and silts), have very high specific surface area to weight ratio, and thus, have a much greater potential to adsorb pollutants than coarser sand particles if equal masses of sediment are involved (Jin et al. 2005). The Guadalupe Estuary samples were characterized by a greater amount of finer silt-sized sediment whereas the Nueces Estuary samples included a greater amount of coarser, sand-sized particles. There were also differences with respect to timing. For example, in the Guadalupe Estuary, dominance of fine particles was observed in October whereas in the Nueces Estuary, July showed the dominance of fine particles. Even though the Nueces Estuary and the Nueces River had generally coarser, average grain size distributions, the adsorption surface area did not vary significantly (Fig. 5.6), and this could be due to the significant number of fine particles in both

estuaries. Thus, there is no difference in the effect of grain size on the adsorption of NH_4^+ ion or organic matter in the sediments of both estuaries.

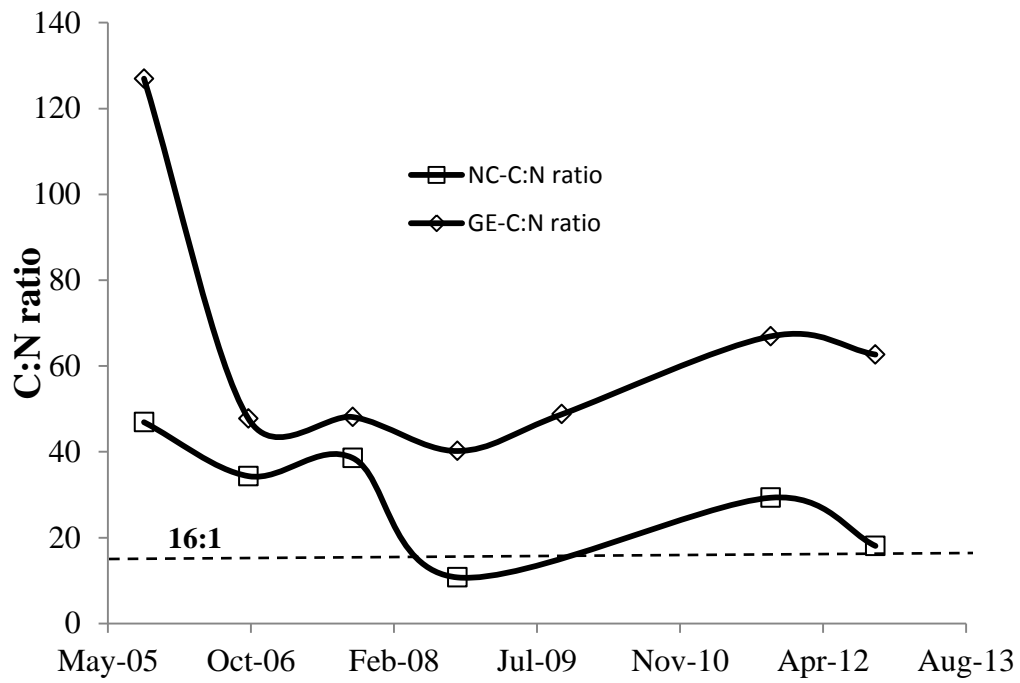


Fig. 5.7 Carbon nitrogen (C:N) ratio at river-estuary mouth of the Guadalupe and Nueces Estuary. Data obtained from Montagna long term data set.

The first order kinetic rate for nitrification in soil is approximately 17 – 20 times higher in sandy loam (0.76 - 1.11) as compared to silty loam (0.048) or clay loam (0.051) soils (Reddy et al. 1984). Nitrification, thus, could be higher in sandy sediment compared to silty loam. That could potentially explain the reason for higher nitrite+nitrate concentrations in the Nueces Estuary treatments versus the Guadalupe Estuary treatments. The increase in nitrate concentration in the Nueces Estuary treatments along salinity gradient might be because of the combined effects of ammonium oxidation in the sandy substrate and favorable condition for nitrifying bacterial community.

In both estuaries, the sediment organic matter in the October samples was slightly higher than in July and January samples. High organic matter in October could be the result of increased inflows that carried higher organic loads into the estuary. Even though the estuary samples collected in the present study showed similar amounts of sediment organic matter, a long term data set (Montagna, unpublished data) shows higher C:N ratios in the Guadalupe Estuary sediments versus Nueces Estuary sediments (Fig 5.7). Sediment nitrogen content was not measured in the samples from this study. However, the high C:N ratio of the Guadalupe Estuary sediments, identified in Montagna long-term data set, indicates a high carbon load that lacks nitrogen. The high C:N ratio could be the reason for low ammonia releases in the Guadalupe Estuary treatments versus the Nueces Estuary treatments.

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CHAPTER VI

CONCLUSION

6.1. Total suspended solids (TSS) and inorganic nutrients

Freshwater inflow (FWI) transports sediments to the Texas Estuaries. However, except during peak inflow events total suspended solids (TSS) did not vary significantly in the estuaries. Besides FWI, frontal events were the significant contributor of TSS in the water. During the cold fronts events the measured TSS was greater than 150 mg/L. In the present study role of FWI and wind in altering TSS concentration identified. TSS measured in the Nueces and Guadalupe Rivers indicates that the Nueces River contributes less in altering TSS concentration versus the Guadalupe River. Even during one high inflow event, i.e., 22 September 2013, when river water flowed over the Calallen Saltwater Dam, at Labonte Park, (Fig 6.1) and had a mean discharge of $193 \text{ ft}^3\text{s}^{-1}$, TSS was higher closer to the Hondo Creek rather than that in the Nueces River (Fig. 6.2). Most of the time, the Nueces River has base flow conditions, thus water does not overflow the Calallen Dam (Fig. 6.3). On 22 September 2013, the average TSS concentration at the station above the Calallen Dam in the Nueces River was 52.45 mg/L, at station next to the confluence of Hondo Creek and the Nueces the TSS was 508.45 mg/L, and while further downstream it was 53.2 mg/L. This indicates that Hondo Creek, which is an ephemeral stream, contributes to the TSS concentration in the river, however, in the Nueces Estuary TSS rarely exceeds 50 mg/L (Fig. 2.4). Lake Corpus Christi may hold most of the sediments resulting lower TSS downstream. In contrast, the Guadalupe River near I-35 (approximately 2 miles upstream of the river-estuary mouth of the Guadalupe Estuary) had average TSS, excluding peak inflow events, was 67.6

mg/L. TSS in the rivers and estuaries may also be contributed by wind. The Aeolian deposit may be an important contributor of TSS and nutrients deposition in the Texas Estuaries. However, in the present study Aeolian deposition has not been studied.

In Texas estuaries, inorganic nutrients decreased since 1987 (Fig. 3.2). One of the main reasons may be because of the lack of sediment inflow to the estuaries. The present study identified a linear relationship between TSS and inorganic nutrients when TSS was greater than 150 mg/L. Because TSS was less than 50 mg/L often, the increase in silicate and orthophosphate concentration increased chlorophyll-a concentration. This indicates at low TSS (i.e. less than 50 mg/L) phytoplankton population uptake the inorganic nutrients while during high TSS concentration inorganic nutrients increased as well. The findings of the present study, thus, identified resuspension as a significant factor in releasing inorganic nutrients. Resuspension by wind and frontal events increased TSS greater than 150 mg/L, which was pivotal on increasing inorganic nutrients. In the Guadalupe Estuary, TSS was highly correlated with ammonia, nitrite+nitrate, and silicate concentration (Table 2.3), and negatively related with salinity. This indicates inflow was the driving force in altering inorganic nutrients and TSS in the Guadalupe Estuary. The principal component analysis result showed seasonal changes are important in altering inorganic nutrients in the Nueces and Lavaca-Colorado Estuaries. The significant positive correlation of silicate concentration with TSS and chlorophyll-a concentrations in the Lavaca-Colorado Estuary indicates resuspension was contributing in fluctuating inorganic nutrients. TSS and chlorophyll-a concentration had positive correlation with silicate and orthophosphate in the Nueces Estuary. The findings of the present study identified that FWI and frontal events are important for the increase in inorganic nutrients in the Texas Estuaries.



Fig 6.1 The Calallen Salt Water Barrier Dam in the Nueces River overflows during high flow events.



Fig 6.2 The Nueces River during peak flow events on September 22, 2013. Right side of the picture showed higher turbidity, which was from Hondo Creek, than from the Nueces River.



Fig 6.3 The Callalen Dam in the Nueces River during most of the sampling time.

6.2. Freshwater inflow and inorganic nutrients

The Lavaca-Colorado Estuary has more inflow than the Guadalupe and the Nueces Estuary. However, its area is more than double to the Guadalupe and the Nueces Estuary, and inflow is more than other two estuaries (Table 3.1). Inorganic nutrients are lower in the Lavaca-Colorado Estuary compared to the Guadalupe Estuary that may be because of the dilution of inorganic nutrients. A field and modeling study identified that the gradient in precipitation and inflow from the Lavaca-Colorado Estuary to the Nueces Estuary has decreased inorganic nutrients concentration in the last 25 years. Climate forecasts by the USGCRP (2009) using a simulation study predicted a decrease in precipitation in South Texas in the future.

6.3 Fluxes of inorganic nutrient in the Sediment-water aerobic layers

In the Guadalupe and Nueces Estuaries, orthophosphate, ammonia, and nitrite+nitrate concentrations were lower than 1 $\mu\text{mol/L}$ during normal base surface flow conditions. However, in the laboratory the 48 hour ammonia released from the Nueces Estuary sediments was greater than 15 $\mu\text{mol/L}$ in most of the samplings, similarly ammonia released from the Guadalupe Estuary was greater than 5 $\mu\text{mol/L}$ in most of the samplings. Even though water column ammonia was less than 1 $\mu\text{mol/L}$ in the Nueces Estuary, the organic matter mineralization was contributing the supply of inorganic nitrogen to the estuary. In the three studied estuaries, silicate was always higher than the half saturation constant concentration i.e., 5 $\mu\text{mol/L}$, referred by Fisher et al. (1988). Besides inflow, the presence of silicate minerals and low grade silica species in the estuaries sediment may be important in order to supply its concentration. In the laboratory setting, orthophosphate concentrations are adsorbed to the sediment with organic matter. The added spike of an extra 5 $\mu\text{mol/L}$ was never detected in water samples, and the adsorption took

place within 5 minutes of addition. As the sediment organic matter was removed the orthophosphate concentration was higher than 15 $\mu\text{mol/L}$ in most of the treatments. The presence of calcite in the sediments may be another factor for the retention of orthophosphate in the treatments with organic matter. The low orthophosphate concentration in the Guadalupe and Nueces Estuary, and immediate drawdown of orthophosphate concentration were most likely to occur in the organic rich estuaries sediment. In the laboratory experiments, turbidity in the sediment solution mixture decreased along salinity gradient (Fig. 6.4). This indicates salinity in the estuary helped in depleting water column orthophosphate by settling clay and calcium mineral particles.

The findings of the present study identified the importance of TSS and inflow volume for the change in inorganic nutrients in the estuaries. Furthermore, inorganic nutrients concentrations were also affected by sediment organic matter and mineral contents. The present study also identified the role of wind for the increase in TSS and inorganic nutrients in the estuaries.

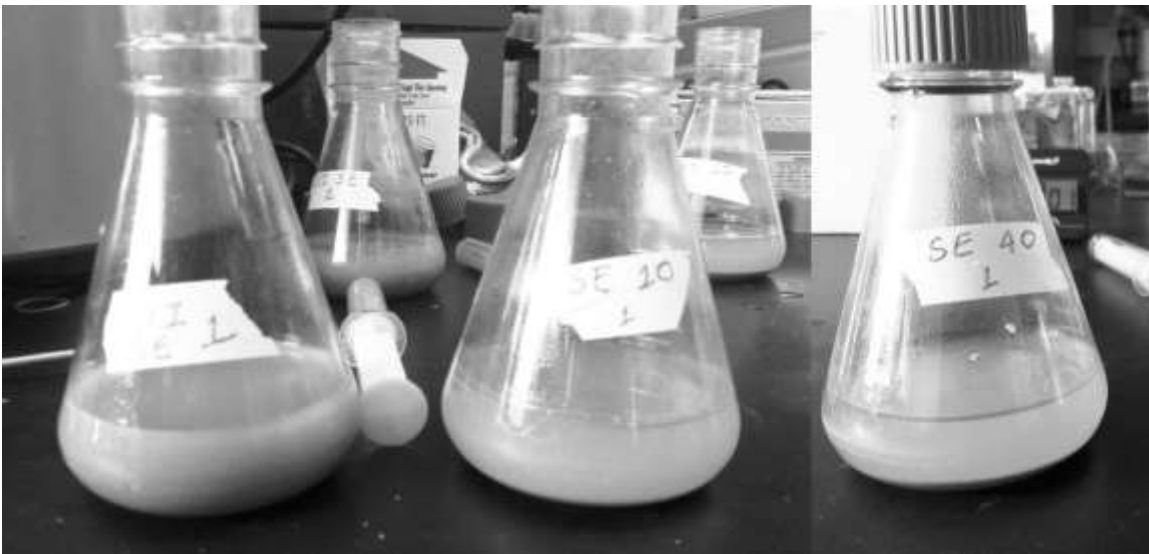


Fig. 6.4 Decrease in turbidity along salinity gradient in the laboratory experiments. Erlenmeyer flask at the left contained sediment in DI water, flask in the middle contained sediment in 7.5 ppt salinity and flask in the right contained sediment in 35 ppt salinity.

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