RELATIONSHIPS BETWEEN NUTRIENTS AND DISSOLVED OXYGEN CONCENTRATIONS ON THE TEXAS-LOUISIANA SHELF DURING SPRING-SUMMER OF 2004

A Thesis

by

SUDESHNA LAHIRY

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

MASTER OF SCIENCE

August 2007

Major Subject: Oceanography

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Approved by:

Co-Chairs of Committee,	Steven F. DiMarco
	Robert D. Hetland
Committee Members,	Ann E. Jochens
	Craig C. Epifanio
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ABSTRACT

Relationships Between Nutrients and Dissolved Oxygen Concentrations on the Texas-Louisiana Shelf During Spring-Summer of 2004. (August 2007)

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Hypoxia (dissolved oxygen concentrations less than 1.4 ml/l) is a recurrent seasonal phenomenon on the Louisiana Shelf, caused by the combined effects of nutrient loading by the Mississippi and Atchafalaya River System (MARS), and density stratification. In 2004, three shelf wide cruises (in April, June and August) were conducted on the Louisiana Shelf to understand the mechanisms controlling hypoxia on the shelf, and examine the relationship between dissolved oxygen and nutrient concentrations during the hypoxic periods. The shelf was divided into three geographically separate zones: A (off the mouth of the Mississippi River), B (off the Terrebonne Bay) and C (off the mouth of the Atchafalaya). Each zone was different in terms of the physical and biochemical processes occurring there. In April, no hypoxia was observed on the shelf because of water column mixing by winds, even though high discharge occurred from the MARS. Nutrients were abundant in the surface waters but present only in little amounts at the bottom. In June, the water column was highly stratified. Because of the presence of upwelling favorable winds no vertical mixing occurred and caused extensive hypoxia on the shelf. Dissolved oxygen concentrations were negatively correlated with nutrients at the bottom of the water column. Nutrients were considerably higher at the bottom than at the surface (except for zone A, where high nutrients were seen even at the bottom), indicating remineralization below the pycnocline. Resuspension of organic material and remineralized nitrogen were sustaining hypoxia far from the river sources. In August, hypoxia was patchy on the Louisiana Shelf. Correlations between dissolved oxygen and nutrient concentration varied seasonally with highest correlations occurring during hypoxic conditions in June and August. The spatial distribution of nutrients and other oceanographic parameters, such as light transmission, fluorescence, and dissolved oxygen concentrations, indicate seasonal variability of biochemical processes that are related to physical processes that affect stratification.

DEDICATION

This thesis is dedicated to my parents, Dipak K. Lahiry and Anuradha Lahiry, my sister, Sumana Lahiry, my grandmother, UmaRani Lahiry and my husband, Shamik Bhattacharya.

ACKNOWLEDGEMENTS

I express my deepest gratitude to my advisor, Dr. Steven F. DiMarco, for his guidance, patience and support throughout my graduate school life. I also thank him for providing the opportunity to go to sea. I am extremely grateful to Dr. Robert D. Hetland, for giving me the opportunity to experience graduate studies in this country. I also thank him for his unvarying support throughout my graduate studies. Special thanks goes to Dr. Ann E. Jochens, for her invaluable comments and constant encouragement, especially during stressful times; and Dr. Piers Chapman for his insightful comments and suggestions. I also thank Dr. Craig Epifanio, for his questions and comments.

Many thanks also to Dr. Matt Howard for data processing and providing access to data. I also thank Dr. Leila Belabbasi for guiding me with the writing of this thesis. I thank all graduate and undergraduate students who helped collect data for this study on three cruises. Thanks also to the ship crew and captain for bringing us safely back to land every time.

I thank the Center for Sponsored Coastal Ocean Research (CSCOR) of National Oceanic and Atmospheric Administration (NOAA), who funded the project (grant # NA03NOS4780039) and provided graduate assistantship and tuition and travel.

I offer special thanks to my parents, grandparents and sister who were always there to support me and were proud at my smallest achievements. Last, but definitely not least, I thank my husband, without whose help I would not have been able to complete this thesis. His support has been immeasurable, especially during the days before my defense and final submission of thesis.

NOMENCLATURE

AOU	Apparent Oxygen Utilization
CTD	Conductivity, Temperature and Depth
GMT	Generic Mapping Tool
MARS	Mississippi and Atchafalaya River System
MCH	Mechanisms Controlling Hypoxia
N	Nitrate
P	Phosphate
Si	Silicate
RC02	Rowe and Chapman 2002

TABLE OF CONTENTS

Page

TABLE OF CONTENTS (CONTINUED)

Page

CHAPTER

LIST OF FIGURES

LIST OF FIGURES (CONTINUED)

LIST OF FIGURES (CONTINUED)

LIST OF TABLES

CHAPTER I

INTRODUCTION

1.1. Background

Hypoxia, defined as dissolved oxygen concentrations in the water column less than 1.4 ml/l (2 mg/l) [*Rabalais et al.,* 2001], is a recurrent phenomenon every summer on the Texas-Louisiana Shelf. The Mississippi - Atchafalaya River System (MARS) drains 41% of the contiguous United States [*Milliman and Meade,* 1983] and discharges high amounts of nutrient rich fresh waters onto the shelf. The combined effect of nutrient loading by the MARS and density stratification results in low oxygen concentrations in waters near the bottom on the shelf. Oxygen depletion typically begins in late April and May, following high discharges from the MARS (but may be as early as February to early March), reaches a peak in midsummer (July) and dissipates by the end of September after fall storms break up the stratification, and allow for oxygen-rich surface waters to mix with oxygen-poor bottom waters [*Turner et al*., 2005, *Rabalais et al.*, 2001].

Low conditions of oxygen are stressful to aquatic life and may cause mass mortality [*Diaz and Rosenberg,* 1995]. On the Texas-Louisiana Shelf, sustained hypoxia may hamper the fishing industry as important fishery resources are affected by direct mortality, forced migration, reduction in suitable habitat, increased susceptibility

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This thesis follows the style and format of *Journal of Geophysical Research*.

to predation, changes in food resources and disruption of life cycles [*Diaz and Solow,* 1999]. Motile fish often vacate the areas affected by hypoxia, while less motile organisms perish [*Rabalais et al*., 2001].

In the Northern Gulf of Mexico hypoxic waters are distributed from shallow depths near shore (4 to 5 m) to as deep as 60 m, but typically are present between 5 and 30 m [*Rabalais et al.,* 2001]. The distance offshore to which hypoxic waters can be found depends in part on the slope of the continental shelf. On the southeastern Louisiana Shelf, where the shelf slopes more steeply towards the deep Gulf of Mexico, hypoxia extends only 55 km from shore. On the central and southwestern Louisiana Shelf, where the continental shelf is broader and the depth gradient is more gradual, hypoxic bottom waters may extend as far as 130 km offshore.

Hypoxia occurs not only at the bottom near the sediments, but well up into the water column. Starting at the bottom, depending on its severity, oxygen depletion may extend into the uppers layers of the water column. Depending upon the depth of the water column, hypoxia may encompass from 10 to 80% of the total water column. Although rare, mid-water column hypoxia is also possible [*Rabalais et al.,* 2001].

Three shelf-wide cruises were performed in Spring-Summer 2004 to survey the conditions during the development, sustenance and dissipation of hypoxia on the Texas-Louisiana Shelf. The survey area was divided into three zones: A (adjacent to the mouth of the Mississippi River), B (off the Terrebonne Bay) and C (off the outflow of the Atchafalaya River). The first cruise in April did not observe any hypoxia. During the second cruise in June, however, hypoxia was observed at all the inshore stations, and a few offshore ones. The final cruise in August observed patchy hypoxia. Nutrient concentrations were highest at the mouths of the rivers (inshore stations), and decreased away moving seaward to the offshore stations in zones A and C. In zone B, nutrient concentrations were less than those in zones A and C. In all three zones, high nutrient concentrations were correlated with low oxygen concentrations in the lower layer, especially during peak periods of hypoxia.

Past programs concerning hypoxia on the Texas-Louisiana Shelf [e.g., *Rabalais et al.*, 2001, *Wiseman et al.*, 1997], were mostly concerned with monitoring the spatial extent of the region affected and assessing the effects of nutrient loading on hypoxia development and intensity. Based on these and other studies, the 'Action Plan for Reducing, Mitigating and Controlling Hypoxia in the Northern Gulf of Mexico' was formulated and sent to the US Congress in 2001 [*Mississippi River/Gulf of Mexico Watershed Nutrient Task Force*, 2001]. The goal of the Action Plan was to reduce the 5-year running average aerial extent of the Gulf of Mexico hypoxic zone to less than 5000 km^2 by the year 2015. This would be made possible by reduction of the nitrogen load to the river by 30%, primarily through voluntary, incentive-based activities.

Phytoplankton consume nutrients to grow. If nutrient availability is limited, then productivity is limited. Because productivity leads to organic matter that consume oxygen when decaying, limitation of nutrients (and the severity of limitation) was thought to be key in inducing hypoxia [*Rabalais et al.*, 2002b]. Although limitation of both silica (Si) and phosphorous (P) does occur, nitrogen (N) limitation was thought to be more frequent and to extend over a larger area. Consequently, the rate of nitrogen loading was believed to be a critical factor in regulating the overall production of phytoplankton. Recent studies by Sylvan et al. [2006], however, suggest that P is the limiting nutrient in phytoplankton growth close to the river mouth. Modeling efforts by Justic et al. [2002], Scavia et al. [2003] and Turner et al. [2005] focus mainly on the biological influences on the Texas-Louisiana Shelf. These studies do not describe the interaction of the physical and biochemical processes that control the size and duration of hypoxia. Rowe and Chapman [2002], however, emphasizes the contribution to hypoxia of physical and biochemical processes in addition to nutrient loading.

For my thesis, I describe the oceanographic conditions and the property distributions on the Texas-Louisiana Shelf during 2004 during the periods of initiation, sustenance and ultimately dissipation of the hypoxic zone. I also examine the correlations between dissolved oxygen and dissolved nutrient (nitrate, phosphate and silicate) concentrations. These concentrations change over the shelf year round based not only on river discharge and seasonal loading variability, but also on the biological processes (e.g., photosynthesis, decay of organic matter and respiration) occurring there. Respiration affects oxygen concentrations at the surface as well as at the bottom of the water column. Some nutrients may be transported out of the source region to other parts of the shelf. I describe the spatial and temporal variability of these correlations to distinguish between regeneration and direct river input. Regenerated nitrogen can be seen at the bottom of the water column during peak hypoxia.

1.2. Hypothesis

In this thesis, I will test one hypothesis. The hypothesis states that, bottom dissolved oxygen was inversely correlated with bottom dissolved nutrients (nitrate, phosphate and silicate) during all three cruises and in all three zones during the hypoxic season of 2004. The null hypothesis states that they were not inversely correlated. For this hypothesis, I will consider all three cruises (April, June and August) and all three zones (A, B and C).

In Chapter II of this thesis, I will present the background information for this study. First, I will discuss the study area. Then, I will discuss the circulation pattern over this area. Next, I will discuss the studies that have been performed in this area, the history of hypoxia, the mitigation plans, and an outline of the development of the new Rowe and Chapman [2002] hypothesis. In Chapter III, I will describe the data sets used for this study and the methodology. In Chapter IV, I will present the results and discussion. Finally, in Chapter V, I will outline the principal conclusions and recommend future work.

This research was supported by the National Oceanic and Atmospheric Administration (NOAA) through the funded project titled 'Mechanisms Controlling Hypoxia on the Louisiana Shelf' (MCH) (grant # NA03NOS4780039, program NGOMEX 2003). The project comprises an integrated, multidisciplinary, numerical and observational study of the competing mechanisms of hypoxia. It investigates the relative importance of both nitrate inputs and physical factors, such as winds, river flow, and local circulation patterns, to the formation and intensity of hypoxia over the eastern part of the Texas-Louisiana Shelf.

CHAPTER II

BACKGROUND

2.1. Study Area

The MARS ranks among the world's top ten in length, freshwater discharge and sediment delivery. Approximately 30% of the total flow from the Mississippi and Red Rivers is diverted into the Atchafalaya River, which eventually discharges near Morgan City, LA, into the Gulf of Mexico, 210 kilometers west of the main Mississippi River birdfoot delta. The remaining 70% is discharged at the birdfoot delta system [*Rabalais et al*., 2002a], see Figure 2.1.

The area of the MCH study consists roughly of a subset of the shelf area affected by the discharges of the two rivers, Mississippi and Atchafalaya (from 89°W to 93°W, north of 28.5°N). This region will henceforth be called the Louisiana Shelf. The study area coincides with the area where hypoxia is likeliest to occur (Figure 2.2) [*Rabalais and Turner,* 2001]. Hypoxia is observed most frequently in the regions off the Mississippi Delta and Terrebonne Bay (indicated in red). In more than 50% of the July survey cruises made by Rabalais and others, hypoxia is seen in the patchy areas off the Terrebonne Bay, the Atchafalaya Bay and Cameron (marked in pink). The study region for the MCH program can be divided into three zones, based on the physical and biogeochemical processes that control hypoxia in each zone [*Rowe and Chapman,* 2002]. The Rowe and Chapman [2002] hypotheses will be discussed in detail later in this chapter.

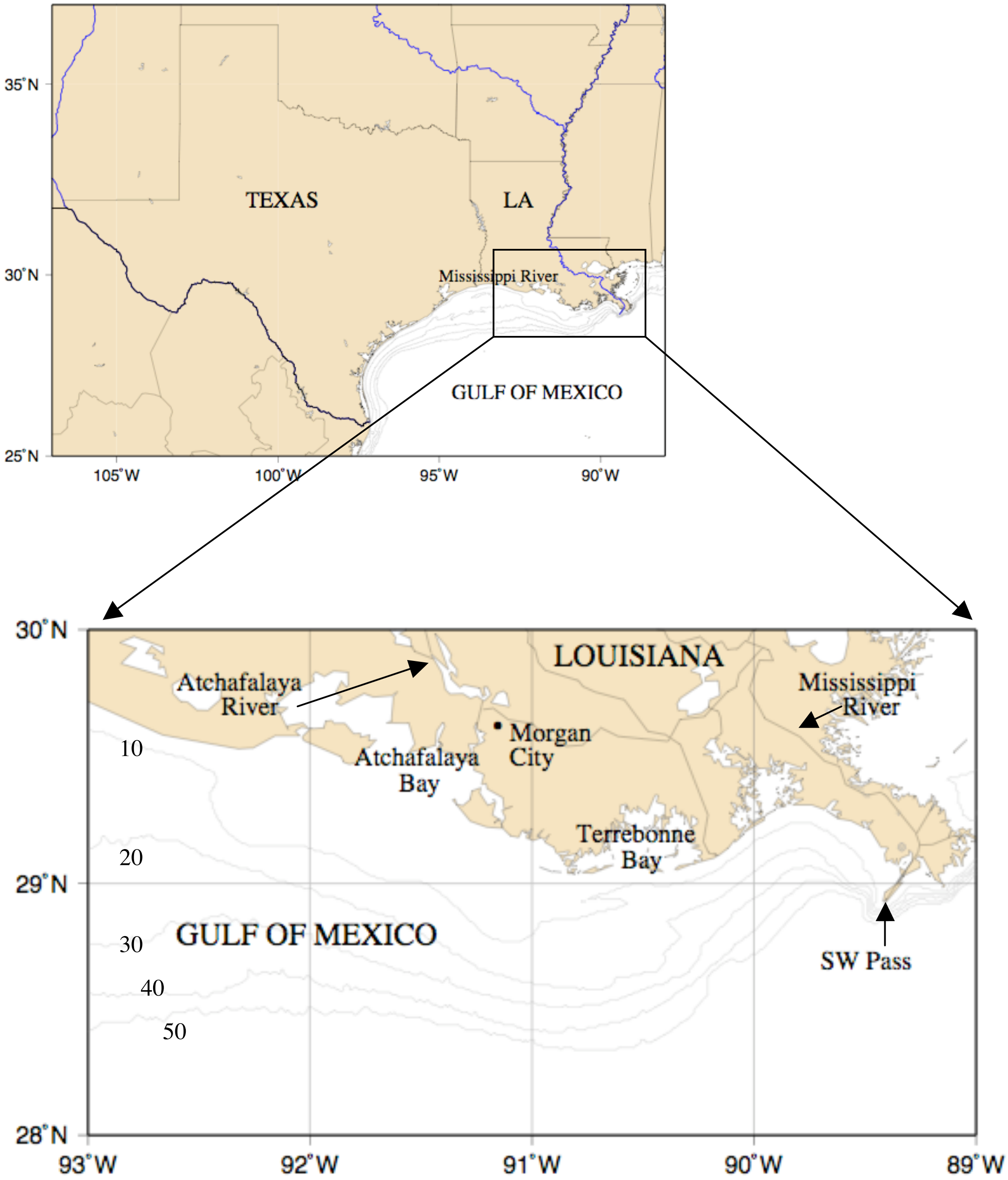

Figure 2.1. Map of study area showing the Mississippi and Atchafalaya Rivers, and their locations in the national scale. Bathymetries shown are 10, 20, 30, 40 and 50 m isobaths.

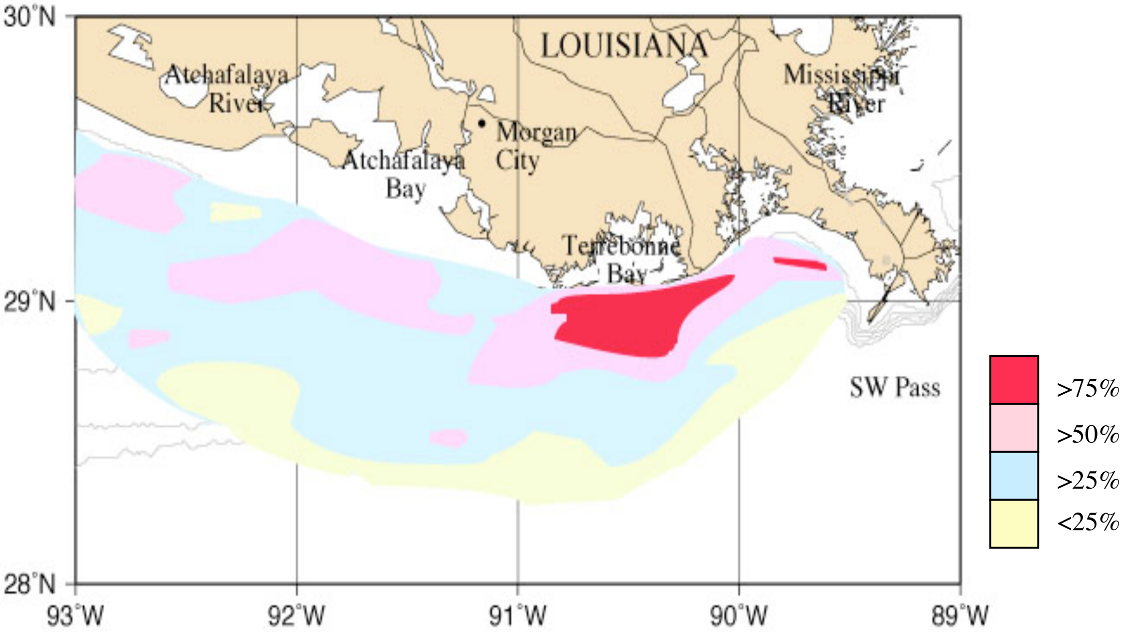

Figure 2.2. Frequency of occurrence of midsummer hypoxia over the Texas-Louisiana Shelf, 1985-2001, after Rabalais et al., [2002]. The region in red is where hypoxia is most frequent, more than 75% of the time. The region in pink is where hypoxia occurs more than 50%, blue > 25% and yellow < 25% of the time.

2.2. Circulation over the Texas-Louisiana Shelf

Currents over the inner shelf (inshore of about the 50-m isobath) are principally forced by alongshelf wind stress, in the pattern hypothesized by Cochrane and Kelly [1986] and confirmed with modification by Cho et al. [1998], Li et al. [1997] and Nowlin et al. [2005]. Currents are typically downcoast (from Louisiana towards Texas) during nonsummer (September through May), transition in June, and are upcoast in summer (June through August). Nowlin et al. [2005] describes an annual signal for salinity due to this circulation pattern, with lowest salinity waters occurring (a) in late spring along the inner portion of the western shelf when downcoast flows carry the high discharges from the MARS and other rivers to the Mexican border, and (b) in summer over the inner and outer eastern shelf when the upcoast flow causes a pooling of the discharges from the MARS over that shelf. Upcoast winds during summer also result in high salinities over the western shelf due to advection from off Mexico and to upwelling. Currents over the outer shelf are variable, but predominantly upcoast throughout the year. Freshwater on the shelf is an important factor affecting both nutrient flux and density stratification, thus playing a major role in the extent and severity of hypoxia.

2.3. Literature Review on Hypoxia Over the Louisiana Shelf

Hypoxia on the Texas-Louisiana Shelf has been documented since 1972 [*Rabalais et. al*., 2001]. The size of the region affected varies from year to year, but the bottom hypoxic area has increased from about 8000–9000 km^2 during 1985–1992 to about 15,000-17,000 km^2 from 1993-1997 (following the Mississippi River Flood of 1993). The aerial extent increased further to about 19,000 km^2 during 1999 [*Ferber,* 2001; *Battaglia and Goolsby,* 2001], and to over 20,000 km^2 in 2001 and 2002. In 1998 and 2000, smaller areas were affected following less than average river discharges, including from a drought in 2000. Other physical factors, such as storms and hurricanes, also tend to reduce the hypoxic area by breaking up the stratification. In the years 2003 and 2005, less than average areas were hypoxic, but 2004 was an average year with about 15040 km^2 affected. In 2006, the area of hypoxia was estimated at 17,200 km^2.

From 1985 to the present, the spatial distribution of hypoxia on the Louisiana shelf was mapped every summer [*Rabalais et al.*, 2001], with 60 to 80 stations between the Mississippi River Delta and westward onto the Texas Shelf. For the period 1985-92, the zone of hypoxia was found to the immediate west of the outflows of the Mississippi and Atchafalaya Rivers. During 1993-2000, hypoxia was extensive over the Louisiana Shelf, with bottom horizontal areas reaching up to 20,000 km^2. The largest aerial extent was seen in 2002 (Figure 2.3).

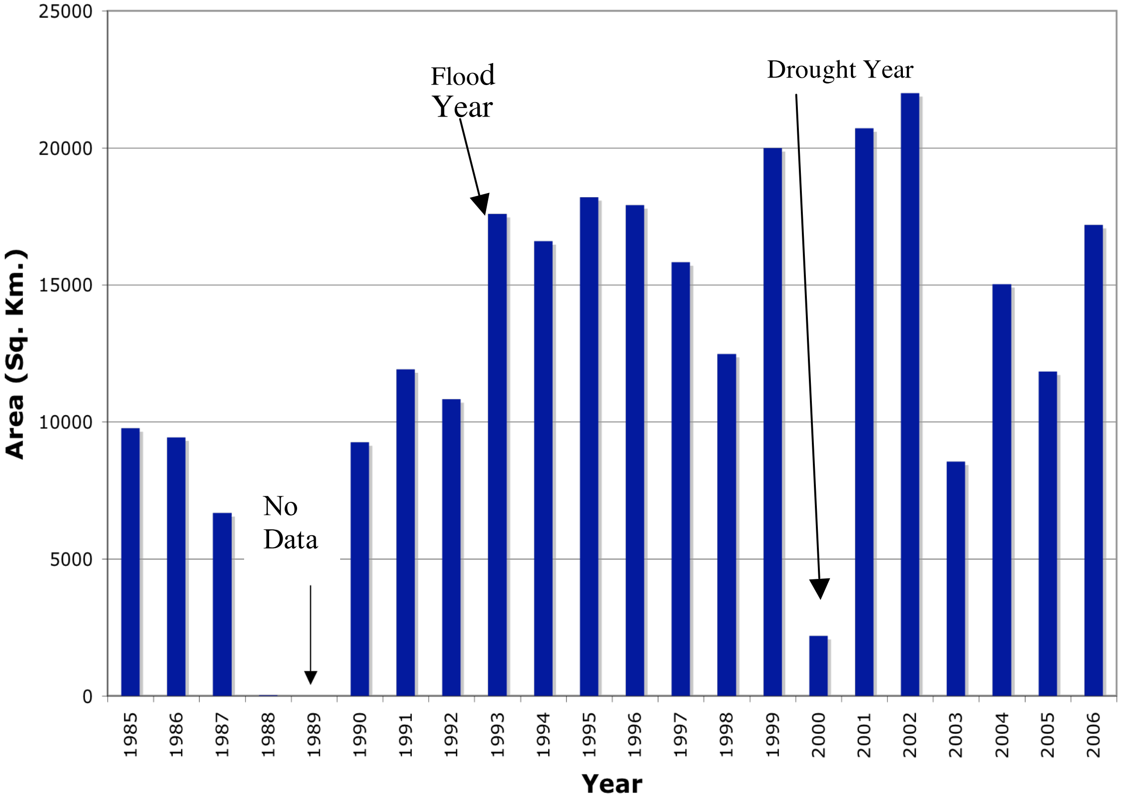

Figure 2.3. Aerial extent of bottom hypoxia for midsummer cruises, 1985-2006. [Data from N. Rabalais, Louisiana Universities Marine Consortium (www. gulfhypoxia .net)].

The aerial extent of hypoxia on the Texas-Louisiana shelf is correlated with the discharge of the MARS [*Wiseman et. al.,* 1997]. He considered the years 1985 to 1996 and found R^2 to be 0.60. However, when the years 1997 to 2006 are considered, the correlation is much weaker. There is a lag of approximately one month between a peak in discharge in the early months of the year, and the formation of hypoxia on the shelf. As a result, low discharge (drought years) decreases the extent of hypoxia on the shelf, while high discharge (floods) increases it. However, the lowest bottom oxygen values are encountered after a 2-month lag from the peak discharge period [*Justic et. al.,* 1993]. Figure 2.4 shows a record of the Mississippi River discharge at Tarbert Landing, MS, from the beginning of January to the end of August 2004. Notice the two spring peaks (February and March) and another peak in June. The red line represents the 70-year mean and the grey line shows the ±1 standard deviations from the mean. The mean flow at this location is high during spring (April) and low during summer (August). During 2004, nearly 5 peaks in discharge were observed, three larger and two smaller. There was high discharge about a month before the first cruise, but low discharge during the cruise. The same can be said about the other two cruises but with different time scales. During these peaks, higher nutrient loading occurred on the Shelf. There was, however, low discharge during April. In fact, it may be stated that the discharge during April of 2004 was uncommon, falling below -1 standard deviation from the mean. The first three peaks though larger than the mean, were within ±1 standard. The fourth peak coincided with the mean. The fifth peak was again, unusual as it rose above the +1 standard deviation from the mean.

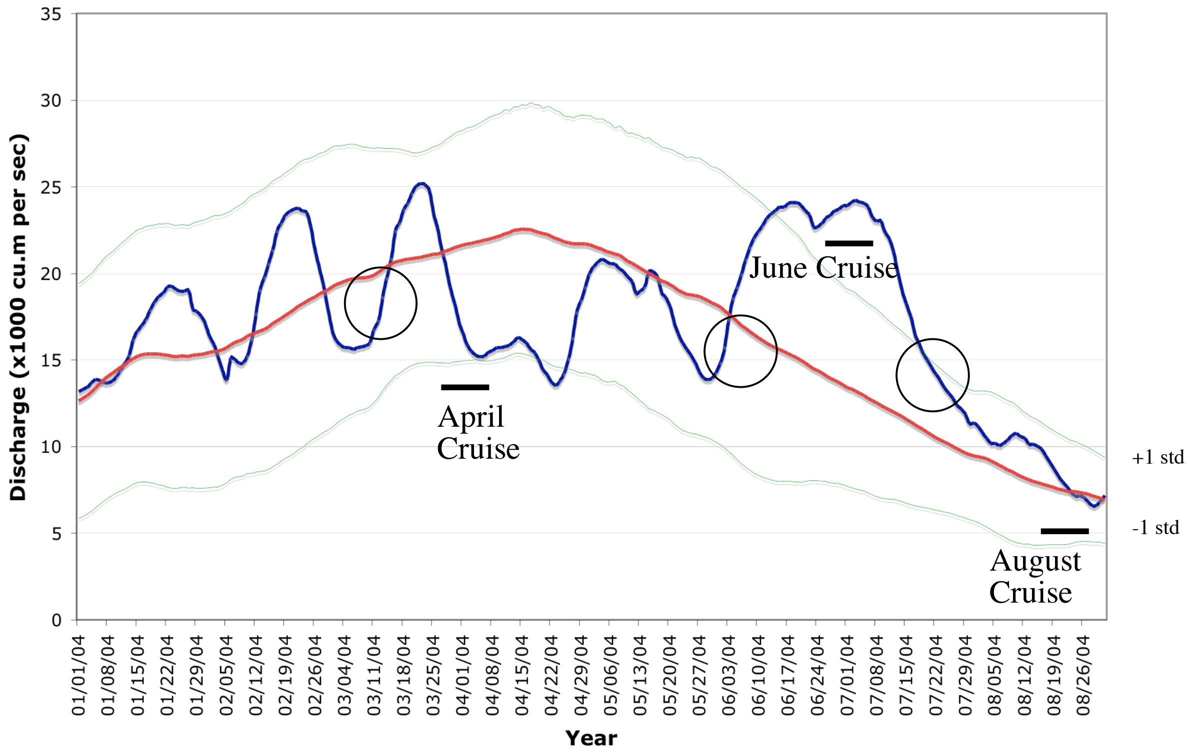

Figure 2.4. Discharge record of the Mississippi River during 2004 (beginning of January to the end of August). Data from United States Corps of Engineers (USCOE) Discharge Data at Tarbert Landing, MS. The blue line shows the discharge; 70-year mean is shown in red, and green shows the ±1 standard deviations. The bars show the duration of the cruises, while the circles show one month prior flow.

Nitrogen input into the Mississippi River drainage basin, primarily from fertilizer usage, has almost doubled since the 1950s [*Rabalais et al*., 2002a]. Although the increase in fertilizer application boosted crop production, it also caused significant increases in riverine nitrate concentrations and flux to the Gulf [*Rabalais et al.,* 2002a; *Goolsby et al*., 1999].

Rabalais et al. [2002b] suggest that while increased nitrogen loads from the Mississippi River system can account for the changes in the hypoxic zone since the 1950s, other factors may contribute to its growth, dynamics and decline. Several of those factors were analyzed and discussed during the scientific and public policy debates leading to the formulation of the Action Plan, [*Mississippi River/Gulf of Mexico Watershed Nutrient Task Force*, 2001]. Those factors include flux of poorly oxygenated waters from the deep Gulf, river loading of organic carbon, river channelization and coastal wetland loss, nitrogen flux from the atmosphere or deep Gulf waters, and climate-induced alterations in water flux from the Mississippi River basin.

The Action Plan emphasized the connection between hypoxia and river nitrogen inputs in general and between hypoxia and increased nitrate loading in particular. The goal was to reduce the 5-year running average aerial extent of the Gulf of Mexico hypoxic zone to less than 5000 km^2 by 2015. This would be done by reducing the nitrogen load to the river by 30%, primarily through voluntary, incentive-based activities, which would include best management practices on agricultural lands, wetlands restoration and creation, river hydrology remediation and riparian buffer strips, and stormwater and wastewater nutrient removal [*Rabalais et. al.,* 2002a].

After the formulation of the Action Plan, several studies were conducted on the limitation of nutrients (and the severity of limitation) which is thought to be key in controlling phytoplankton blooms, and hence hypoxia (for example, *Rabalais et al.*, 2002b). Sylvan et al. [2006] suggest that P reduction strategies should also be included in the Action Plan to reach the goal of reduction of hypoxia on the Texas-Louisiana Shelf.

Recent modeling studies were conducted in the post-Action Plan years by Justic et al. [2002], Scavia et al. [2003] and Turner et al. [2005], which aimed at predicting the aerial extent of the hypoxic zone. Turner et al. [2005] used Total Kjeldahl Nitrogen (TKN) to develop a predictive relationship between the presences of TKN in surface waters to concentrations of bottom water oxygen. TKN is an analysis to determine the amount of total organic nitrogen contained in water. Although this model failed to predict the area resulting from the drought conditions in 1988, it was successful for other years and yields an R^2 of 0.79. The other two models also examined the relationship of the riverine fluxes and bottom hypoxia on the Shelf. The Scavia et al. [2003] is a one-dimensional dissipation model with inputs of oxygen utilization rates and nutrient loading. Physical processes are modeled empirically and bundled into a single advection term that has no temporal variability. The Justic et al. [2002] uses a two box modeling study to show that riverine nutrient fluxes, via their influence on net productivity of the upper water column, play a major role in controlling the development of bottom water hypoxia and accumulation of organic carbon in coastal sediments. Physical processes include only vertical oxygen flux across the pycnocline but do not mention net horizontal transport.

The Action Plan and the above-mentioned studies, however, did not fully address the relative role of the magnitude of physical processes that are known to exist on the shelf and can be important in initiating and sustaining hypoxia in the Gulf of Mexico. Although some of the studies mention stratification as an important aid to formation of hypoxia, there is no quantification of how much or how little is required to sustain hypoxia on the Louisiana Shelf. To address these deficits in the Action Plan and other studies, Rowe and Chapman [2002], here after called ‘RC02’, postulated their hypothesis that physical and other biogeochemical processes in addition to nutrient loading contribute to hypoxia on the Louisiana Shelf (Figure 2.5). Belabbassi [2006] establishes a lower limit on the Brunt- Väisälä (BV) frequency of 40cph to initiate hypoxia based on data taken during the summers 1992-1994 between Brownsville, TX and Southwest Pass, LA. The Brunt-Väisälä frequency is the natural frequency at which a particle of fluid displaced vertically in a fluid will oscillate about its original position [*Brunt*, 1927 and *Väisälä*, 1925].

According to RC02, the region of a continental shelf around a river source can be divided into three process-oriented zones that depend on the different physical and biochemical processes that occur there. In the brown zone, nearest to the river mouth, hypoxia is controlled by chemistry and turbidity. Light penetration is low which leads to low primary production. Sedimentation rates are high as the particulate organic carbon carried by the river is flocculated out. (Flocculation refers to a process where fine particulates are caused to clump together in a solution in the form of flakes, which may then settle to the bottom of the solution.) Respiration in the sediments is essentially anaerobic, which produces ammonium, sulfides, and compounds of reduced iron and manganese.

The green zone immediately adjacent to the brown zone is the zone of highest primary production in the surface waters. Light penetration is high, as much of the Particulate Organic Carbon (POC) has flocculated out in the brown zone; nutrient concentrations (nitrate, phosphate and silicate) are high, though not higher than those compared to the values found near the mouth of the rivers (brown zone). Initial decomposition of organic matter in the sediments is aerobic, but as production continues above the pycnocline and oxygen in the lower layers is consumed, hypoxia and anaerobic respiration are initiated.

The blue zone, according to RC02 is spatially the largest and is most affected by the volume of fresh water discharged by the rivers. Stratification plays an important role in this zone. Nutrient concentrations in the surface layer are low because of consumption in the green zone, and production is controlled by regenerated nitrogen. Respiration at the bottom is aerobic, with little organic carbon deposition and little denitrification. All three zones are affected by the changes in the freshwater input, hydrography and wind forcing.

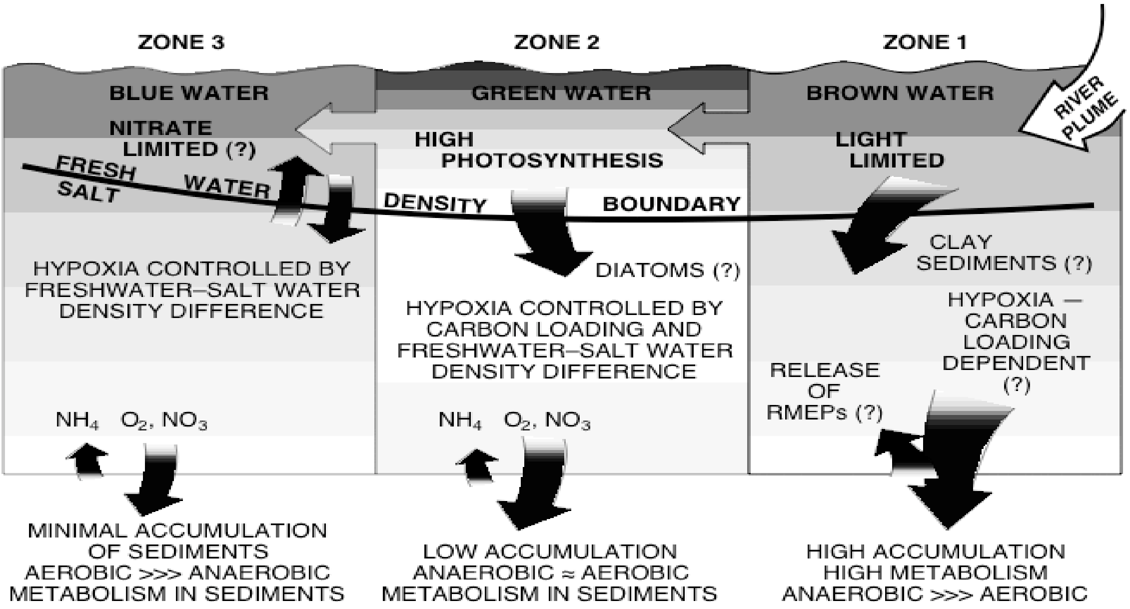

Figure 2.5. The Rowe and Chapman hypotheses describing the physical and biochemical processes that initiate and sustain hypoxia on the Texas-Louisiana Shelf, [*Rowe and Chapman*, 2002]. Reprinted with permission of Gulf of Mexico Science.

The RC02 zones are not tied to a specific geographic region on the Louisiana Shelf. They may be formed anywhere on the shelf according to the physical and biochemical processes governing them. The zones may be of different sizes; one may be larger than the other. If suitable conditions persist, they may even be transformed from one zone to another at the same geographic region. However, this transformation may occur only from zones A to B and A to C, not vice versa, [*DiMarco et al.*, submitted 2007].

CHAPTER III

DATA AND METHODS

3.1. Data

The purpose of this chapter is to describe the data that were collected for this study and the methods used to analyze the data. Field data were collected on three shelf wide cruises. The ancillary data were downloaded from various websites.

3.1.1. Field Data

Three research cruises were conducted on the *R/V Gyre* during April, June and August of 2004. Station locations are shown in Figure 3.1. A summary of the cruises is provided in Table 3.1. Each cruise conducted about 18 hydrographic stations in each of the three general regions of the shelf and several stations between the regions. The regions marked A, B and C corresponds roughly to RC02's brown, green and blue zones, respectively. However, the RC02 zones are not restricted to geographical boundaries, but depend on the physical and biochemical processes occurring at the mouths of the rivers. The cruises lasted about seven days each.

Measurements at each station included those using Niskin bottles (12 bottle rosette, each having a capacity of 10-15 l), CTD (instrument measuring conductivity, temperature and depth), bottom-tripped Niskin bottle (known as the Pogo), and a surface bucket. The Pogo is much like the CTD/rosette system, but smaller, with only four, 5-l Niskin bottles, a CTD and a transmissometer. At each station, first the CTD/Niskin bottles were deployed, followed by the Pogo. Measurements of dissolved oxygen concentration, salinity and dissolved nutrient concentrations (nitrate, nitrite, ammonium, urea, silicate and phosphate) were drawn from the Niskin bottles from the water column and analyzed on board. Oxygen concentrations were determined using the Winkler titration method, salinity concentrations using a Salinometer and nutrient concentrations using a 6-channel Autoanalyzer. The bottles were tripped at depths with 5-m spacing. The Pogo bottles were tripped at about 0.75 m above the bottom. The bucket was used to draw samples from the surface for analysis of salinity and nutrients. Measurements between the zones were done on the 10-m and 20-m isobaths. Table 3.2 provides a summary of the data that were collected on each of the cruises.

Table 3.1. Cruise summaries for 2004.

Cruise ID	Start Date	End Date	Number of Stations
MCH1	2 April 2004	8 April 2004	59
MCH2	25 June 2004	1 July 2004	61
MCH3	19 August 2004	26 August 2004	78

The *R/V Gyre* had a flow-through system, which provided measurements of near-surface temperature, salinity, and chlorophyll fluorescence in near-real time (2 minute intervals). Continuous flow-through sampling used water from an in-line flow that was

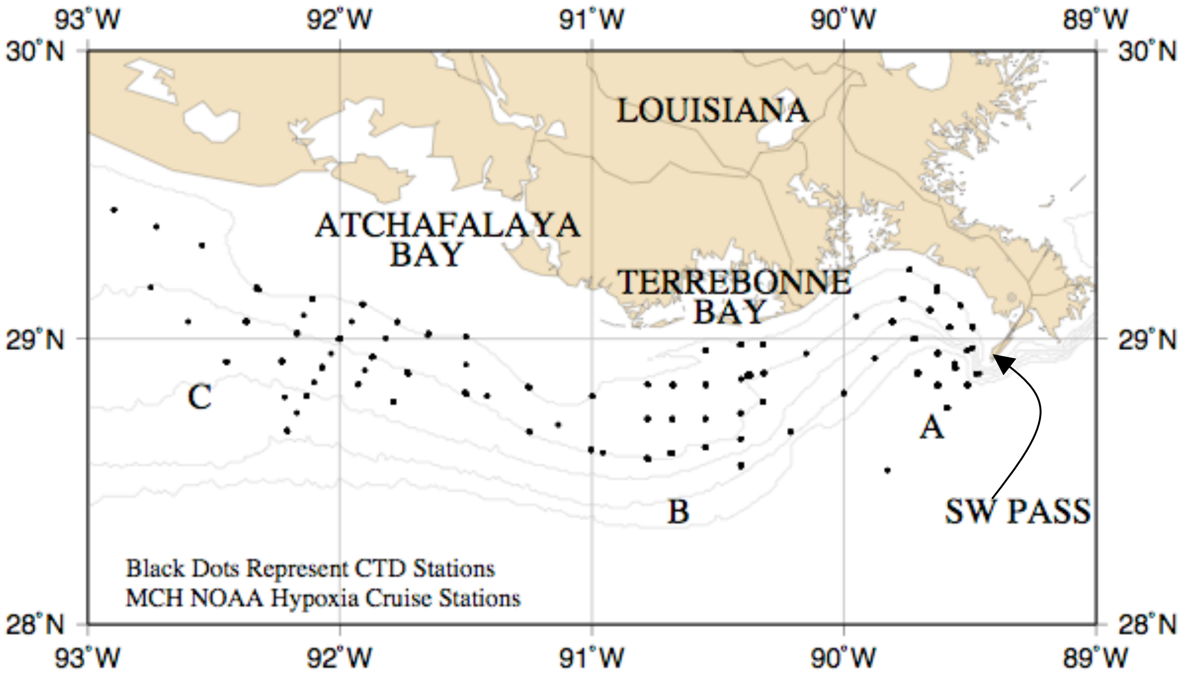

Figure 3.1. Map showing all the stations during the three cruises in 2004. The three zones, Brown (A), Green (B) and Blue (C) are marked on the map. Bathymetries shown are 10, 20, 30, 40 and 50 m isobaths.

Table 3.2. Station summary of the three 2004 cruises.

Property	MCH1	MCH2	MCH3
Dissolved Oxygen	59	61	78
Nutrients	59	59	78
CTD	59	61	78
Pogo			
DO	59	61	78
Salinity	59	61	23
Nutrients	59	61	74
Bucket			
Salinity	59	0	74
Nutrients	55	60	74
Fluorometer	Continuous (2 min interval)	Continuous (2 min interval)	Continuous (2 min interval)
Thermosalinograph	Continuous (2 min interval)	Continuous (2 min interval)	Continuous (2 min interval)

Table 3.3. Summary of measurements taken from instruments on the CTD frame.

Property	Instrument	Make/Model
Fluorescence	Fluorometer	Chelsea Aqua 3
Dissolved Oxygen	Oxygen Probe	SBE 43
PAR/Irradiance	PAR Sensor	Biospherical/Licor
% Transmission	Transmissometer	Chelsea/Seatech/Wetlab CStar
CTD	Seabird	SBE-911-Plus
Optical Back Scatter	OBS Seatech	Seatech LS6000

pumped from the ship's hull depth of 3.5 m to laboratory sensors. These flow-through data were not used directly in this thesis.

The CTD/Rosette frame was equipped with a transmissometer, an OBS (Optical Back Scatter, which determines the concentration of suspended solids in the water column), a fluorometer and a PAR sensor (Photosynthetically Active Radiation, which designates the spectral range of solar light from 400 to 700 nanometers that is useful to plants in the process of photosynthesis). The measurements taken with the various sensors are summarized in Table 3.3.

3.1.2. Ancillary Data

In addition to cruise data, other data were collected from other sources. These data include:

1. River discharge data – I have used the Mississippi River Discharge data at Tarbert Landing, MS. These data are made available by the US Army Corps of Engineers. The location of this gauge (ID 01100) is on the Mississippi River near river mile 306.3. This gauge collects daily discharge data. The URL is – 'http://www.mvn.usace.army.mil/cgi-bin/wcmanual.pl?01100'.

2. Sea Surface Height data - Source is Colorado Center for Astrodynamics Research (CCAR), Real-Time Altimetry Project, University of Colorado. Sea Surface Height maps are produced from Jason, TOPEX/POSEIDON (T/P), Geosat Follow-On (GFO), ERS-2 and Envisat altimeter data processed in near real-time, usually within 12 to 36 hours of overflight. An analysis product is based on the latest 10 days of Jason and T/P, and 17 days of GFO and 35 days of ERS-2 sampling, if available. Data are available at:

‘http://argo.colorado.edu/~realtime/gsfc_gom-real-time_ssh/’. Data are courtesy of Dr. R. Leben, CCAR.

3. Wind data – The wind data were obtained from the archives of the National Data Buoy Center (NDBC) Coastal-Marine Automated Network (C-MAN) station GDIL1, in Grand Isle, LA. The C-MAN stations have been installed on lighthouses, at capes and beaches, on near shore islands, and on offshore platforms. Data collected at C-MAN stations typically include barometric pressure, wind direction, speed and gust, and air temperature. These data are processed and transmitted hourly to users in a manner almost identical to moored buoy data. The GDIL1 station is located at 29.27 °N 89.96 °W. The data can be downloaded from – ‘http://ndbc.noaa.gov/download_dataphp ?file name=gdil1c2004.txt.gz\&dir=data/historical/cwind/’.

3.2. Methodology

The GMT (Generic Mapping Tools) software package [Wessel and Smith, 1991] was used to produce gridded values and contoured fields of horizontal and vertical profiles of oxygen, Apparent Oxygen Utilization (AOU), salinity, temperature, density, chlorophyll, and nutrients (nitrate, phosphate and silicate only). GMT is a free, public domain software package that can be used to manipulate columns of tabular data, time-series, and gridded data sets, and display these data in a variety of forms such as simple x-y plots and maps. GMT software is written as a set of UNIX scripts and is totally self-contained and fully documented. All input to be used for GMT analysis were prepared using UNIX scripts. GMT was also used to make maps of the study area.

For all the other analyses, MATLAB was used. MATLAB is a high-level technical computing language and interactive environment for algorithm development, data visualization, data analysis, and numeric computation. Information regarding MATLAB can be found at 'http://www.mathworks.com'.

Statistical computations performed were:

- Mean, standard deviations and maximum/minimum ranges of dissolved oxygen, AOU, salinity and nutrients
- Correlations between AOU and nutrients, oxygen and nutrients, and between pairs of nutrients
- Ratio analysis, like Redfield Ratio, total nitrogen and phosphate, total nitrogen and silicate, total nitrogen and oxygen, phosphate and oxygen, and silicate and oxygen.

Values of AOU were computed using MATLAB scripts written by Edward T. Peltzer of Monterey Bay Aquarium Research Institute (MBARI) and modified to suit the current situation. AOU is used to illustrate the distributions of nutrients. AOU was obtained by subtracting the observed value of oxygen in the water column from the saturated value [*Takahashi et al.*, 1998]. Thus, a value of 0 for AOU means that the water is completely saturated with dissolved oxygen. Supersaturated waters show negative values, while positive AOU's indicate unsaturated waters.

Total Nitrogen concentrations were computed by adding the concentrations of nitrate, nitrite, ammonium and urea. Particulate organic and inorganic nitrogen, molecular nitrogen and dissolved organic nitrogen were not included in total nitrogen calculations.

CHAPTER IV

RESULTS AND DISCUSSIONS

In this chapter I will display and discuss the results from each cruise. For each cruise, I will first describe the oceanographic conditions during the cruise. Next, I will show the property distributions and finally discuss the correlations between oceanographic properties.

4.1. April Cruise

4.1.1. Oceanographic Conditions

The April cruise was conducted from 2 – 8 April 2004. Figure 4.1 shows the near-real time sea surface height conditions based on satellite altimeter data in the Gulf of Mexico on April 5, 2004. The Loop Current is the dominant circulation feature in this figure and is indicated by high sea surface height (red). The Loop Current however, does not penetrate north of 27°N, and, therefore, does not impact the circulation of the study area directly.

In the Gulf of Mexico, there generally is a lag of approximately one month between a peak in the Mississippi discharge measured at Tarbert Landing, MS, and the peak formation of hypoxia on the Texas-Louisiana Shelf [*Wiseman et. al.,* 1997]. Following heavy rains in March 2004, there was high discharge (> 25 x 10^3 m^3s^{-1}) from the Mississippi River into the Gulf of Mexico just prior to the April cruise. However, there was no hypoxia found during this cruise. This is because both nutrient loading and stratification are essential for the formation of hypoxia in the northern Gulf of Mexico.

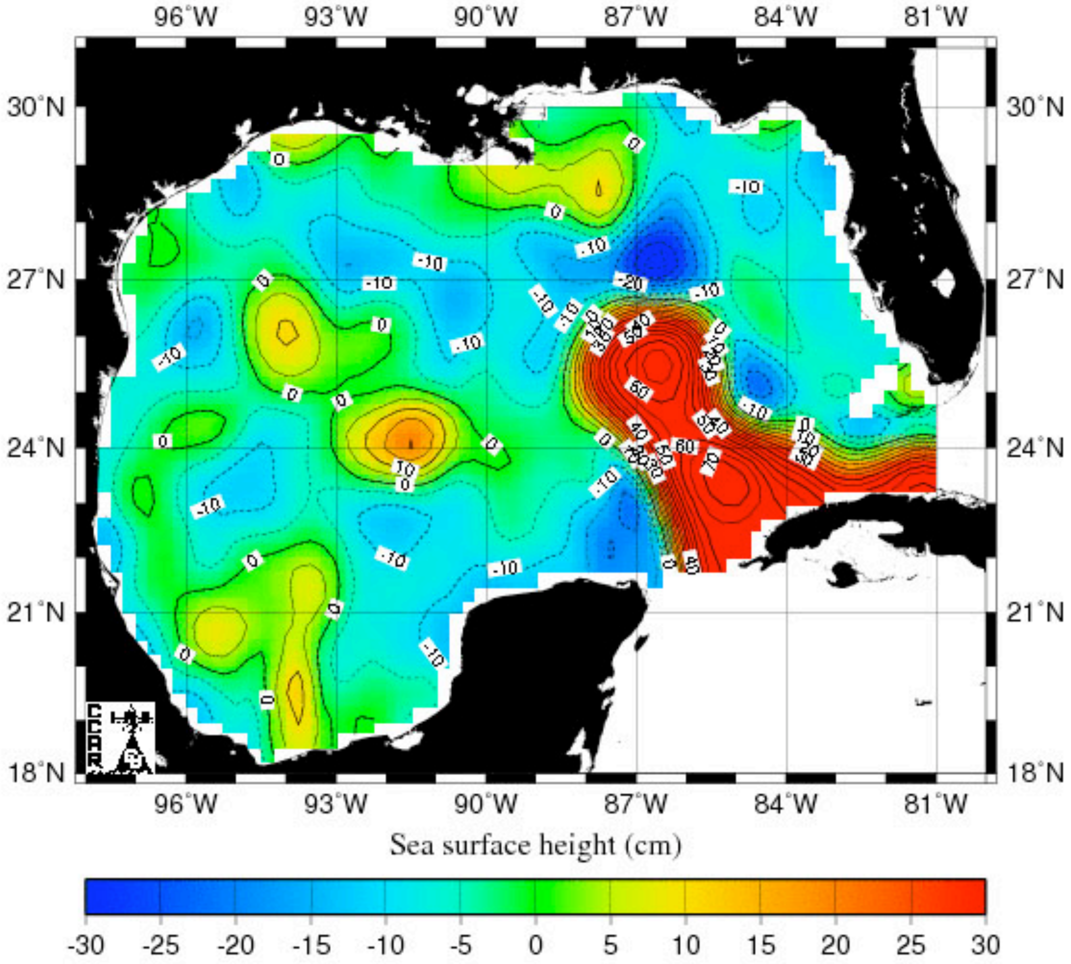

Figure 4.1. Sea surface height of the Gulf of Mexico on April 5, 2004. (Figure courtesy of Dr. R. Leben, Colorado Center for Astrodynamics Research, Dept. of Aerospace Engineering Sciences, University of Colorado). URL: http://argo.colorado.edu/~real time/ gsfc_gom-real-time_ssh/.

During this cruise, however, despite the high nutrient loading, the water column was well mixed, as there were winds and frequent spring storms maintaining a homogeneous, unstratified water column. It is generally understood that altimeter data in the coastal zone is not reliable due to aliasing of the land signal into the altimeter footprint.

4.1.2. Property Distributions During April 2004

The properties measured on this cruise were oxygen, salinity, nitrate, phosphate and silicate concentrations using bottles and CTD probes as described in Chapter III. The contoured maps of these properties at the bottom and surface of the water column are included in appendix A (A1 through A11).

Figure 4.2 shows the distribution of oxygen concentrations in the bottom meter of the water column. Typical bottom oxygen values during this cruise ranged from 3 to 6 ml/l (recall ≤1.4 ml/l being hypoxic). Near the outflow of the Mississippi and Atchafalaya Rivers at the inshore stations of zones A and C, waters were not saturated with oxygen below the pycnocline, but saturated above the pycnocline at the surface, implying the presence of the river plume. Nutrients, fluorescence and light transmission confirmed this. The saturation was greater in zone A than in zone C due to closer proximity to the river mouth. Both above and below the pycnocline, concentrations decreased offshore. At the offshore stations in zones A and C, surface waters were supersaturated due to photosynthesis by phytoplankton. In zone B, waters were unsaturated both above and below the pycnocline. Oxygen concentrations were highest in the surface waters of zone A, with highest concentration being 9.603 ml/l. Zones A and C receive fresh waters directly from the MARS, while zone B receives fresh waters through the westward advection of the Mississippi River discharge and the eastward advection of the Atchafalaya River discharge.

Light transmission was low at the surface at the inshore stations of zones A and C (about 40%), indicating the presence of particulate matter discharged into the ocean with the river freshwater. At the offshore stations, however, transmission increased to 65% as particulate matter settled out of the water column. Surface transmission in zone B was quite high (90%). Fluorescence was highest at the offshore stations in zone A and lowest in zone B. Fluorescence is indicative of the amount of chlorophyll in the water, so high fluorescence in zone A indicated phytoplankton productivity.

Salinity values were lowest near the outflows of the Mississippi and Atchafalaya Rivers, and increased oceanward. At the surface, salinities near 10 salinities were found close to the Southwest Pass and increased to typical oceanic values of 35-36 at the offshore stations. Lowest salinity values in the surface were in the zone A; zone C (especially in the stations off the mouth of the Atchafalaya) had values of about 20, which then increased offshore. Surface salinity values were lower than bottom values at all three zones (stratified water column). At the bottom, salinities ranged from about 20 to 35-36. As expected, lowest values were found just off the outflow of the Mississippi River, with values of 10-12.

High nitrate concentrations are seen near the outflows of the Mississippi and Atchafalaya Rivers; highest in zone A and lowest in zone B. The highest concentration of nitrate was observed in zone A at an inshore station (27.43 μM/l) at the surface, close to the Southwest Pass. Nutrient concentrations were high at all the inshore stations of zone A and at most of the inshore stations of zone C, indicating the presence of the river plumes. Away from the river outflows and towards the offshore stations in zones A and C, nitrate concentrations decreased, as nutrients were consumed by phytoplankton during production. In zone B, very low concentrations were found at the surface. Below the pycnocline, higher concentrations were seen, suggesting regeneration in small amounts. In an attempt to identify regeneration, ammonium values were analyzed from samples beneath the pycnocline and near the bottom of the water column. High ammonium concentrations would suggest regeneration processes. A small increase in ammonium concentration was also seen at the bottom, especially in the western part of zone B, which strongly suggests regeneration below the pycnocline. A summary of all the nutrient concentrations is provided in Table 4.1.

Phosphate concentrations were smaller compared to nitrate concentrations in all three zones, both at the surface and at the bottom. This is not surprising, since phosphate input to the shelf is typically much smaller than that of nitrate. The highest concentration of phosphate was 2.97 μM/l and was seen in zone A. In all three zones, concentrations were higher at the inshore stations and decreased offshore. Concentrations at the surface were generally higher than those at the bottom. Nitrate to phosphate ratios were very high in zone A (highest being 40.21) indicating that this was a phosphate limited system.

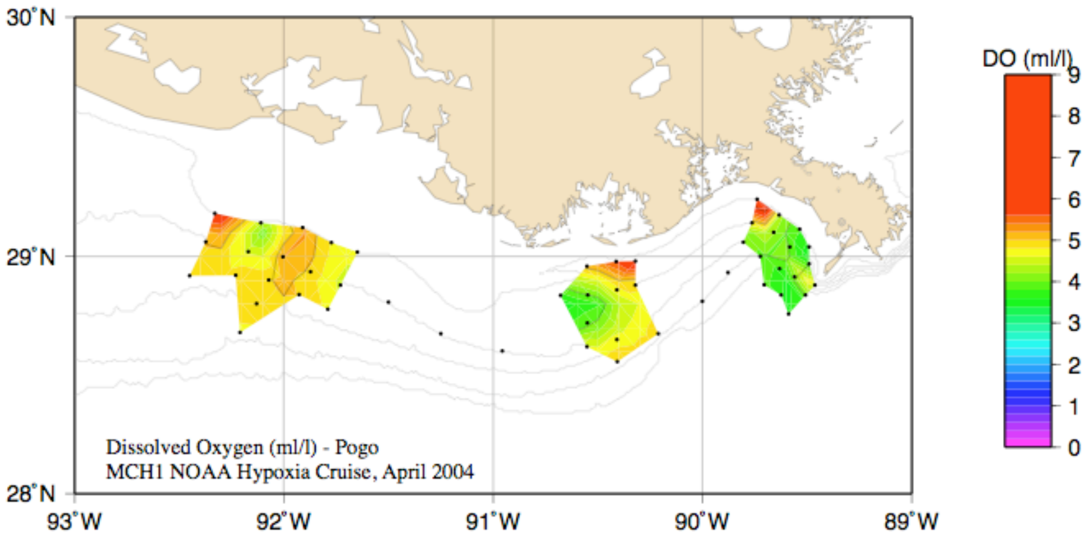

Figure 4.2. Bottom dissolved oxygen concentrations (ml/l) during the April 2004 cruise (MCH1). Bathymetric contours shown are 10, 20, 30, 40 and 50 m isobaths.

Surface silicate concentrations were highest at the inshore stations of zones A (20 μM/l) and C (10 μM/l) due to the presence of the river plume. At the offshore stations, concentrations decreased to about 5 μM/l. Perhaps this is because diatoms consumed silicate during production in the area, but this is mere speculation. In zone B, silicate concentrations were lowest at the surface. At the bottom, concentrations were high in all three zones.

Table 4.1. Basic statistics of nutrient values during the April 2004 cruise. bd = below detection.

Nutrient	Maximum (μM/l) / Zone	Minimum (μM/l)	Average (μM/l)
Total Nitrogen	31.97 / C	0.03	2.78
Nitrate	28.62 / C	bd	2.27
Phosphate	2.97 / A	0.03	0.49
Silicate	35.42 / C	bd	5.55

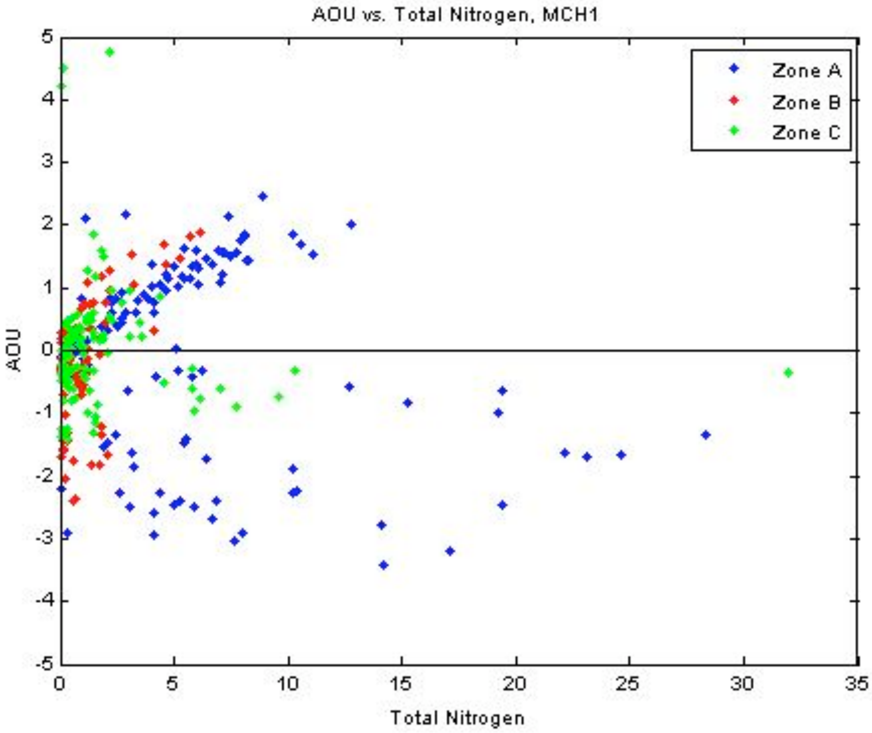

Figure 4.3. AOU (ml/l) vs. total nitrogen (μM/l) concentrations during the April cruise, 2004. Blue, green, and red dots indicate measurements at zones A, B, and C, respectively.

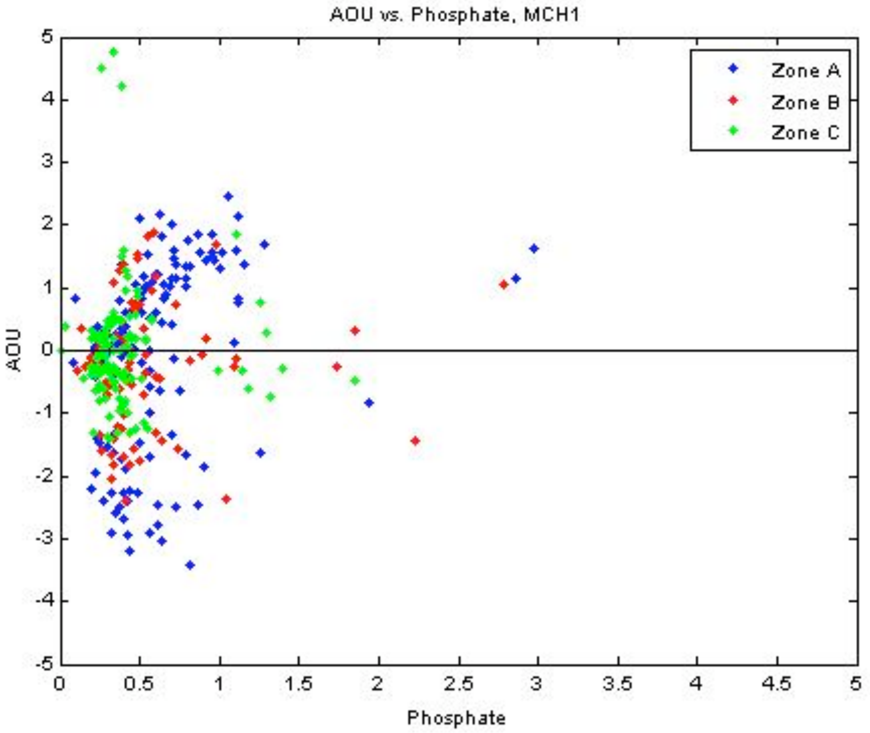

Figure 4.4. AOU (ml/l) vs. phosphate (μM/l) concentrations during the April cruise, 2004. Blue, green, and red dots indicate measurements at zones A, B, and C, respectively.

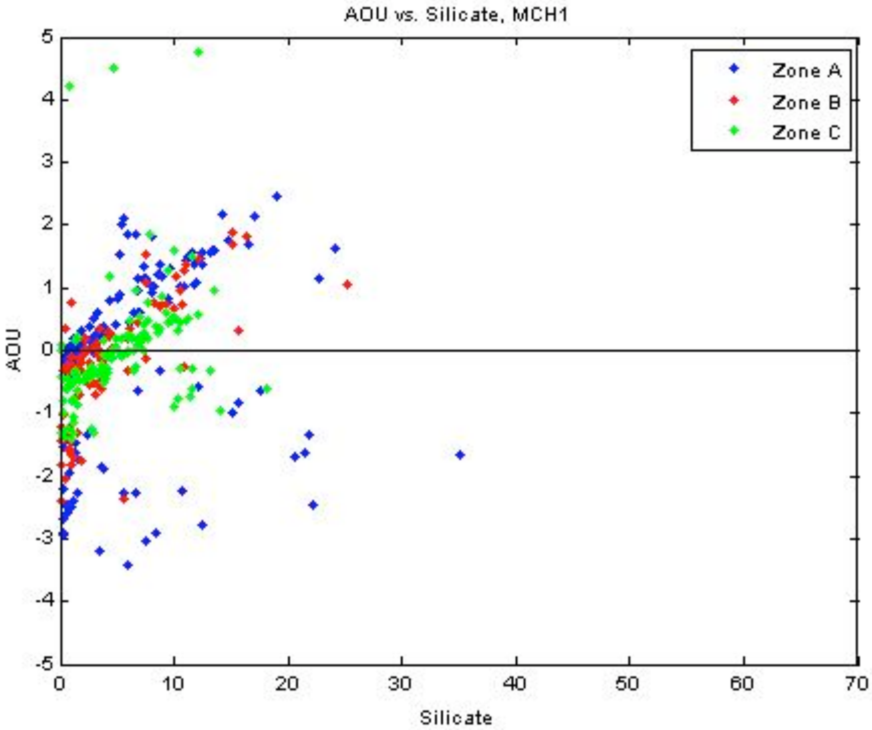

Figure 4.5. AOU (ml/l) vs. silicate ((μM/l) concentrations during the April cruise, 2004. Blue, green, and red dots indicate measurements made at zones A, B, and C, respectively.

AOU concentrations were helpful in confirming what biochemical processes were occurring on the shelf. For example, at the stations closest to the rivers, AOU ranged from about +1.0 to +2.5 (ml/l). A phytoplankton bloom in the surface waters would likely increase the amount of dissolved oxygen, which would be evidenced by large negative AOU values. Below the pycnocline, benthic processes requiring oxygen, i.e., respiration, would lead to unsaturated values. AOU values would then necessarily be positive. For the case of hypoxia, high positive AOU values would be expected. In Figures 4.3 and 4.5, we see that high nutrients correspond to large negative AOU and were related to the stations located near the river plume. In zones A and C, at these stations, there was likely photosynthesis occurring leading to oxygen release into the water column at the surface. Here, there was no fixed relationship between oxygen concentrations and nutrients due to the variability in biological uptake and light limitation. Away from the river plume at the offshore stations, high nutrients were seen in unsaturated waters both above (zone A) and below (zones B and C) the pycnocline. If these samples are isolated out and a correlation is performed, we expect a more linear relationship than simply correlating all parameters at all depths. In case of both total nitrogen and silicate, low concentrations were seen in zone B above the pycnocline. Below the pycnocline in unsaturated waters, higher concentrations of both nutrients were seen as a result of remineralization processes.

Figure 4.4 shows the distribution of AOU versus phosphate in the water column. The effect of the river plume is evident here in zones A and C, with negative AOU and significant nutrient concentrations. However, phosphate concentrations are much less than either nitrate or silicate, indicating a phosphate limited system. Above the pycnocline there was no well-formed relationship with oxygen due to differential biological uptake. Below the pycnocline too there was no linear relationship. It is not clear as to why phosphate concentrations were more variable than total nitrogen and silicate concentrations. However, it may be that biological processes and speciation differed significantly during this cruise and were not differentiated in the data collected.

4.1.3. Correlations

As stated in the previous section, I have considered the correlation for all unsaturated points. This will be useful in establishing relationships between oxygen and the nutrients, and among the nutrients below the pycnocline. Above the pycnocline, different processes cause the relationships to be more complicated. During the first cruise, the correlation coefficient between total nitrogen and phosphate was 0.29, which was significant at 95% level of significance [*Emery and Thomson*, 1997]. The other correlations are summarized in Table 4.2. The results from the bulk correlation show that oxygen was negatively and significantly correlated with total nitrogen and silicate. The magnitude of the correlation was small, i.e., less than 0.4. The correlation of oxygen and phosphate was not significant, and when the data was separated into zones, the relationships between properties and geographic location is more clear. Total nitrogen and silicate correlates well with oxygen in zone B only. In zone C, however, the correlation is not significant, due to differential biological uptake. Phosphate was not significantly correlated with oxygen in any of the three zones because Phosphate was the limiting nutrient and was not being remineralized below the pycnocline.

Table 4.2. Summary of correlations during the April 2004 cruise. Correlation coefficients in bold indicate significance at 95% level.

			Correlation Coefficient, R		
Property 1	Property 2	(All un-saturated points)	Zone A	Zone B	Zone C
Oxygen	Total Nitrogen	**-0.37**	**-0.35**	**-0.89**	-0.006
Oxygen	Phosphate	-0.12	-0.20	0.0009	-0.05
Oxygen	Silicate	**-0.28**	-0.29	**-0.77**	-0.05
Total Nitrogen	Phosphate	**0.29**	**0.47**	-0.02	0.22
Total Nitrogen	Silicate	**0.53**	**0.64**	**0.74**	0.28
Phosphate	Silicate	**0.42**	**0.79**	0.19	0.09

The nutrients were all significantly and weakly correlated with each other. However, looking at individual zones, the correlation is strongest in zone A and ceases to exist in zones B and C. In zone A, the correlations are likely the result of influence of the river loading. However, it is interesting that in zone B, only silicate is positively and significantly correlated with nitrogen. In zone C, none of the nutrients are significantly correlated probably as a result of differential biological uptake.

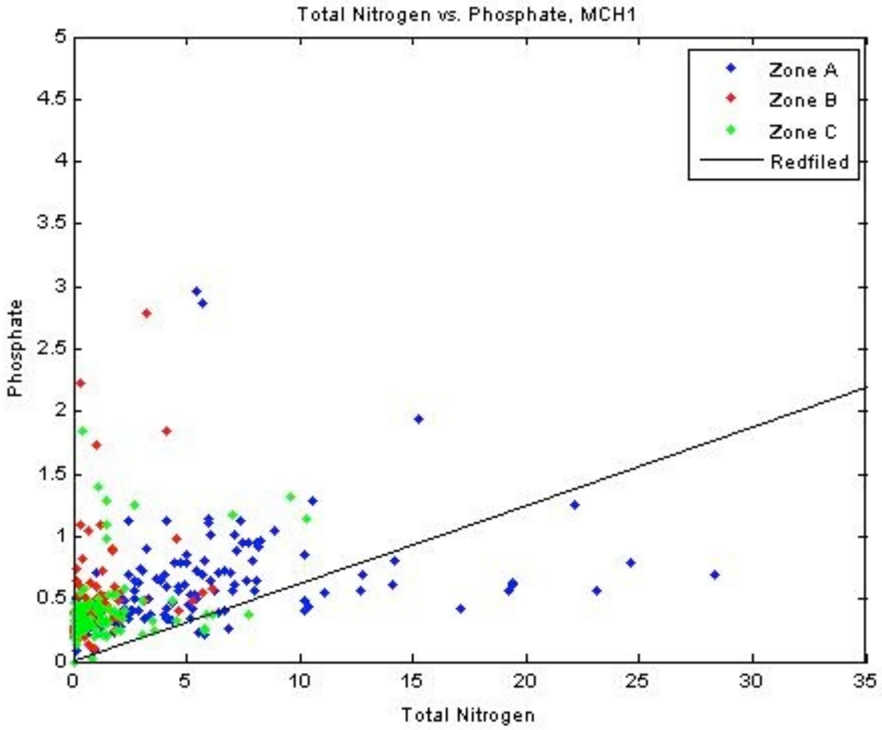

Figure 4.6. Total nitrogen (μM/l) vs. phosphate (μM/l) plot for April cruise. Color of dots indicate spatial region of data collection.

Figure 4.6 shows the ratio between total nitrogen and phosphate . the slanted solid line is the 16:1 Redfield Ratio line. High values of total nitrogen and phosphate ratios are seen only in zone A indicating a deficit of phosphate compared to total nitrogen in the surface waters. This zone, therefore, may be termed phosphate-limited. Above the pycnocline, two processes, namely nutrient loading and eutrophication were affecting the nitrate to phosphate ratio, while biological decay and regeneration of nutrients was typically affecting this ratio below the pycnocline. Above the pycnocline, the river discharges nutrients into the water column. Much less phosphate was discharged compared to nitrates, making the system phosphate limited. Biological uptake was also depleting phosphates fast from the surface waters. Below the pycnocline, the organic matter was decaying and introducing nutrients back into the water column. There are more components in total nitrogen in addition to these in the ocean, like Dissolved Organic Nitrogen (DON) and particulate nitrogen that were not measured during these cruises. If all of these components were measured, the ratio between total nitrogen and phosphate would probably have been in accordance with the Redfield Ratio.

4.2. June Cruise

4.2.1. Oceanographic Conditions

The second cruise was conducted from June 25 through July 2, 2004. Figure 4.7 shows the near real-time sea surface height conditions in the Gulf of Mexico on June 28, 2004. As seen in the April cruise, the Loop Current is present to the southeast. A weak anticyclone is present just north of the Loop Current. Neither of these features, however, directly affect the circulation in the study area on the Louisiana Shelf.

About two months prior to this cruise (in May), there was a peak in discharge from the Mississippi River into the Gulf of Mexico. Hypoxia was extensive hypoxia was witnessed on the Shelf during this cruise. Figure 4.8 shows the hypoxic stations in red. 25 of 59 stations were hypoxic. Virtually all the inshore stations were found to be hypoxic as were a few offshore stations. Winds were very light during this cruise, which enhanced strong stratification and discouraged mixing of the water column.

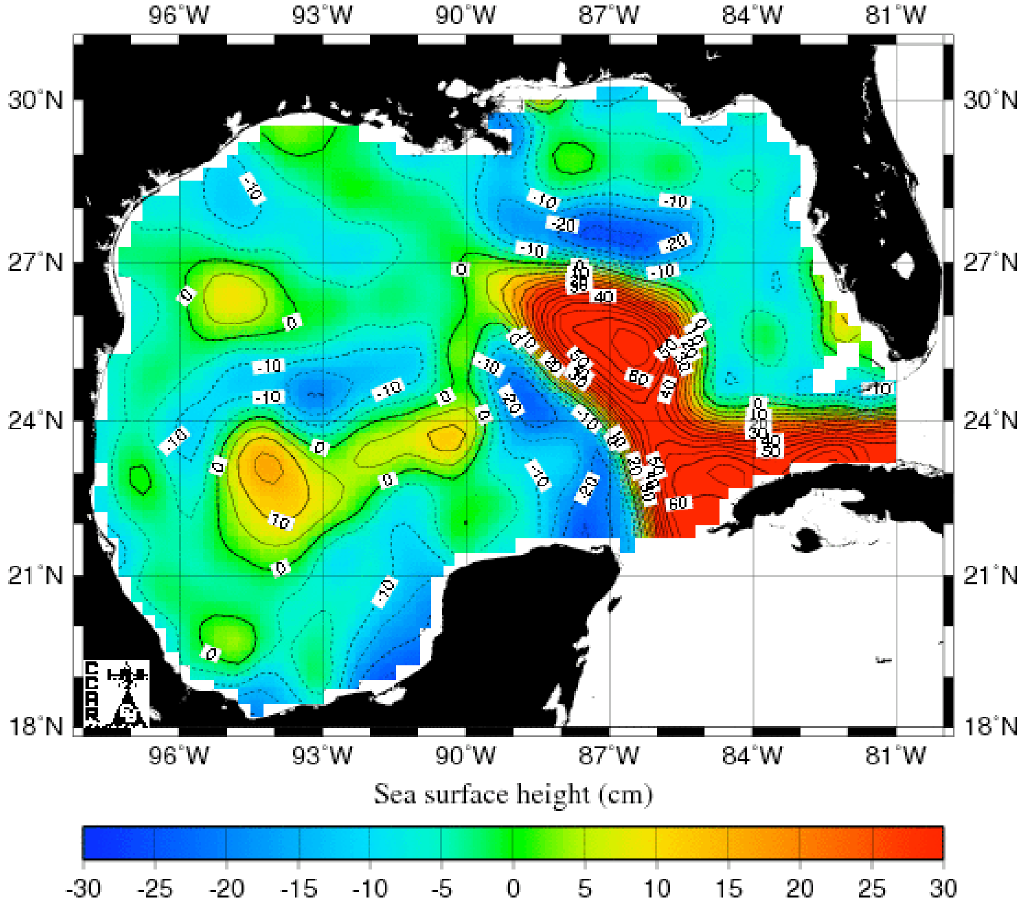

Figure 4.7. Sea surface height of the Gulf of Mexico on June 28, 2004. (Figure courtesy of Dr. R. Leben, Colorado Center for Astrodynamics Research, Dept. of Aerospace Engineering Sciences, University of Colorado). URL: http://argo.colorado.edu/~realtime/gsfc_gom –real-time_ssh/.

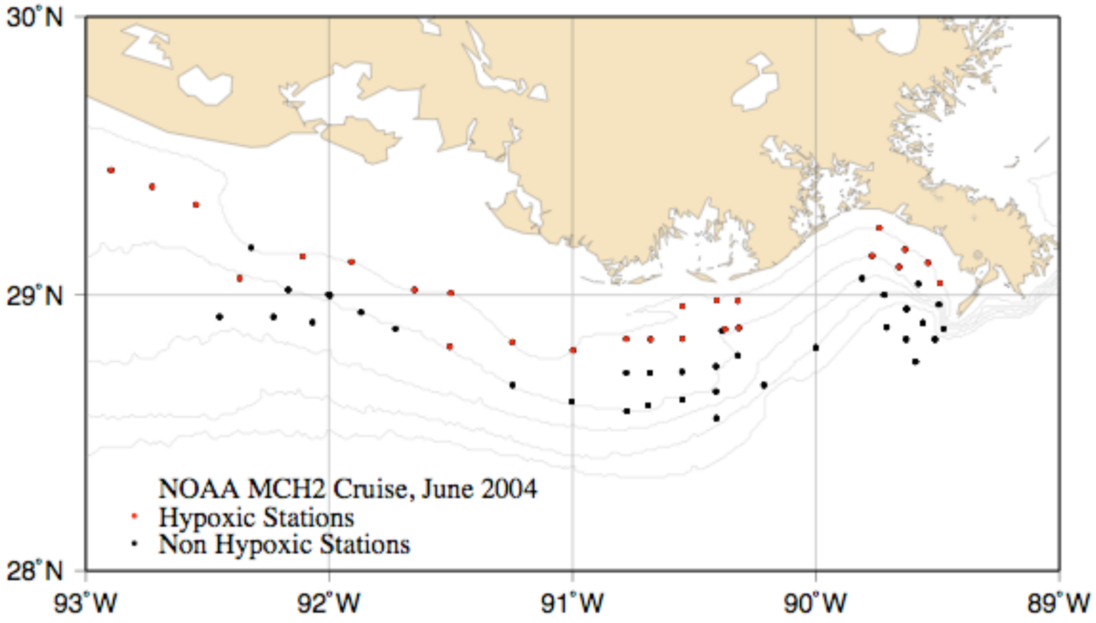

Figure 4.8. Summary of hypoxic stations during the June cruise in 2004. The red dots represent stations that were hypoxic while the black dots represent the non-hypoxic stations.

4.2.2. Property Distributions During June 2004

Of the three cruises considered in this study, the lowest value of oxygen was seen in the bottom meter of the water column during this cruise: 0.05 ml/l, Figure 4.9. This value was measured south of the Atchafalaya Bay in zone C, along the 20 m isobath. Near the outflows of both the Mississippi and Atchafalaya Rivers, lowest oxygen concentrations were seen. In zone A, oxygen concentrations at the bottom increased away from the coast towards the offshore stations. In zones B and C hypoxia extended to the offshore stations particularly in zone BC (between zones B and C). As expected, surface oxygen values were higher than bottom values, with the highest being 6.77 ml/l in zone B. At the surface, waters were saturated with oxygen and concentrations were lowest at the inshore stations and higher at the offshore ones. About four offshore stations had saturated oxygen concentrations at the surface and hypoxia at the bottom. Surface light transmission in zone A was extremely low at about 20% (due to the presence of particulate matter associated with the fresh water plume) while surface transmission was high in zones B and C. At the bottom, however, transmission was low in all zones, with zone B being the lowest (~ 20%). This suggests resuspension of particulate material at the bottom of the water column.

Salinity concentrations were similar to those found on the first cruise. The freshest waters were seen off the outflows of the rivers at the inshore stations, while more saline waters were seen offshore. Also, as expected, surface waters were fresher

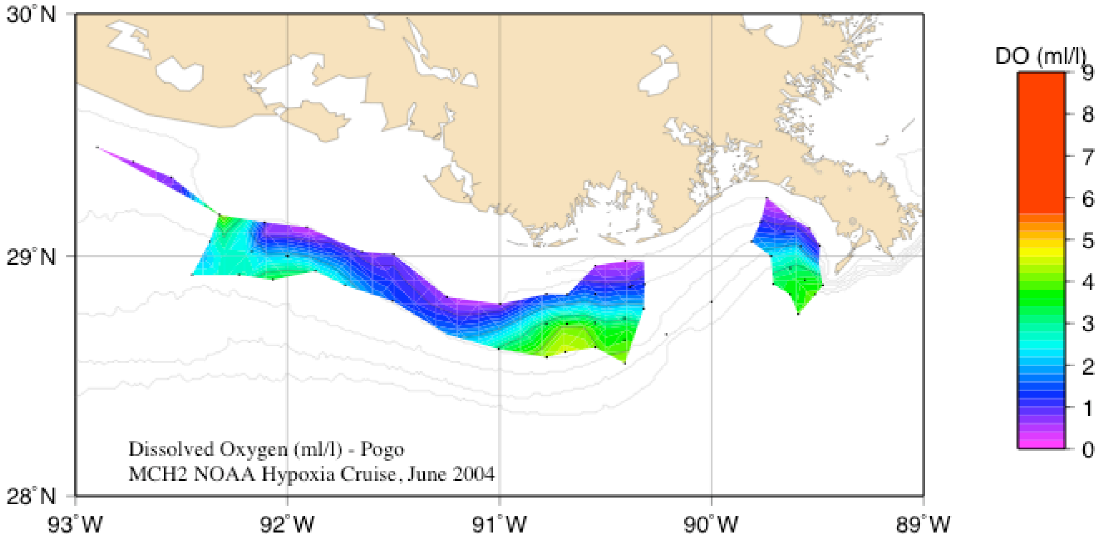

Figure 4.9. Bottom dissolved oxygen concentrations (ml/l) during the June cruise (MCH2). Bathymetric contours shown are 10, 20, 30, 40 and 50 m isobaths.

than bottom waters. The maximum salinity observed was 36.44 in zone B at an offshore station while the minimum salinity of 9.10 was in zone A off the mouth of the Mississippi delta at Southwest Pass.

During this cruise, very high total nitrogen concentrations were seen, especially near the river sources. Four stations very close to the mouth of the Mississippi River were seen to have total nitrogen concentrations in excess of 70 μM/l, the highest reaching 103.15 μM/l. The next highest total nitrogen concentration (not including these four stations) was 35.83 μM/l in zone A. Highest concentration in zone A were at the surface, with much lower concentrations at the bottom; inshore stations had higher concentrations than offshore stations. In zone B, higher concentrations were seen at the surface than at the bottom at the inshore station, but at the offshore stations the concentrations were low both above and below the pycnocline. Between zones B and C and at zone C however, very high concentrations were seen at the bottom with very low concentrations at the surface. Concentrations in zone C were much smaller compared to zone B. The concentrations of high nitrogen below the pycnocline between zones B and C and zone C were being produced in situ via regeneration. This was confirmed by the high concentrations of ammonium being present there.

Phosphate concentrations were very small at the surface, but higher at the bottom. Highest phosphate value (3.95 μM/l) was seen in zone B below the pycnocline excluding the four stations near Southwest Pass. The basic statistics of bulk concentrations for the June cruise are given in Table 4.3. Nitrate, silicate and phosphate mean concentrations were highest during this cruise relative to April and August.

Table 4.3. Basic statistics of nutrient values during the June 2004 cruise. bd = below detection.

Nutrient	Maximum (μM/l) / Zone	Minimum (μM/l)	Average (μM/l)
Total Nitrogen	35.83 / A	bd	7.37
Nitrate	34.83 / A	bd	5.90
Phosphate	3.95 / B	0.01	0.46
Silicate	53.36 / A	bd	10.58

Silicate concentrations were highest (maximum of 53.36 μM/l) at the surface at the inshore stations in zone A. At the offshore station stations, they were much lower (about 5μM/l). In zones B and C, concentrations were higher at the bottom than at the surface.

In Figures 4.10 and 4.12, we see effect of the river plume on nutrient concentration in zone A, which is characterized by high total nitrogen and silicate concentrations and large negative AOU. Regeneration was seen to occur below the pycnocline, where there is large positive AOU and high nutrients. Many of these samples were hypoxic. In the unsaturated samples, total nitrogen concentrations were highest in zone A and silicate concentrations were highest in zone C. Zone B had small amounts of nitrate above the pycnocline that was from the river discharge. Below the pycnocline, there were high amounts of both nitrate and silicate in zone B resulting from

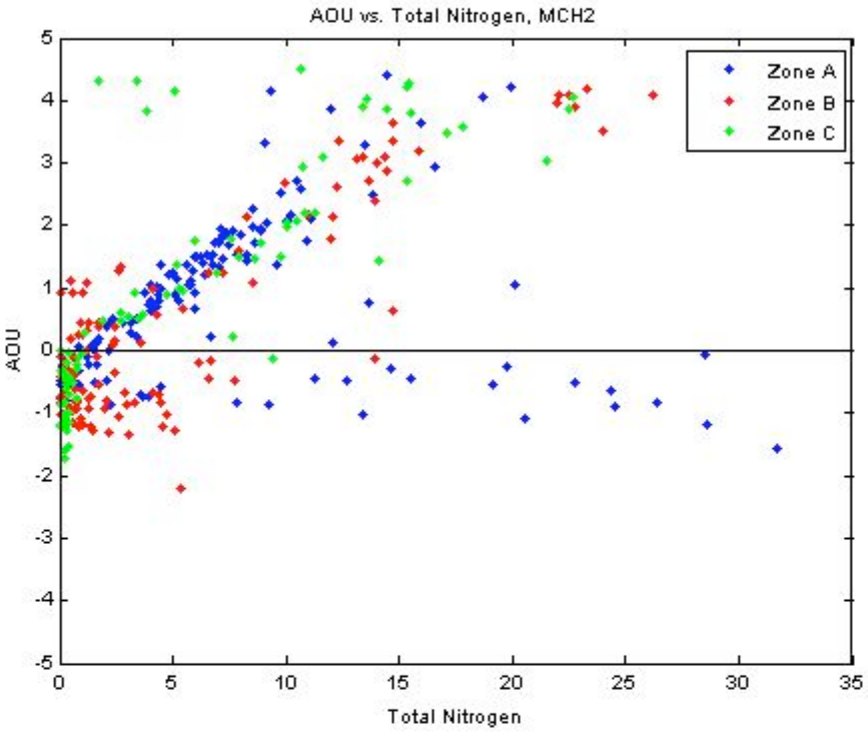

Figure 4.10. AOU (ml/l) vs. total nitrogen (μM/l) concentrations during the June cruise, 2004. Blue, green, and red dots indicate measurements made at zones A, B, and C respectively.

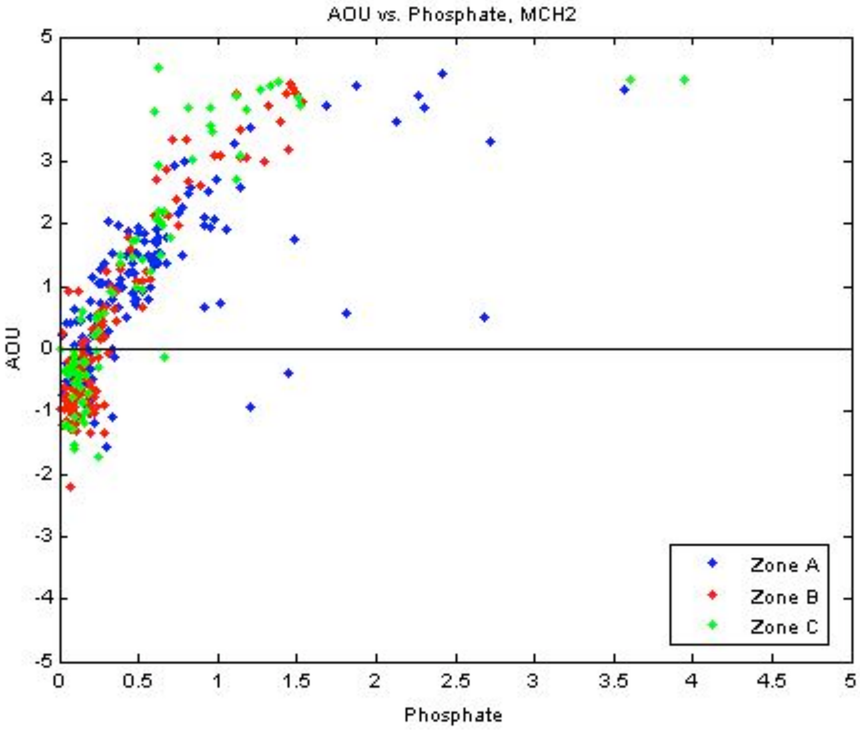

Figure 4.11. AOU (ml/l) vs. phosphate (μM/l) concentrations during the June cruise, 2004. Blue, green, and red dots indicate measurements made at zones A, B, and C respectively.

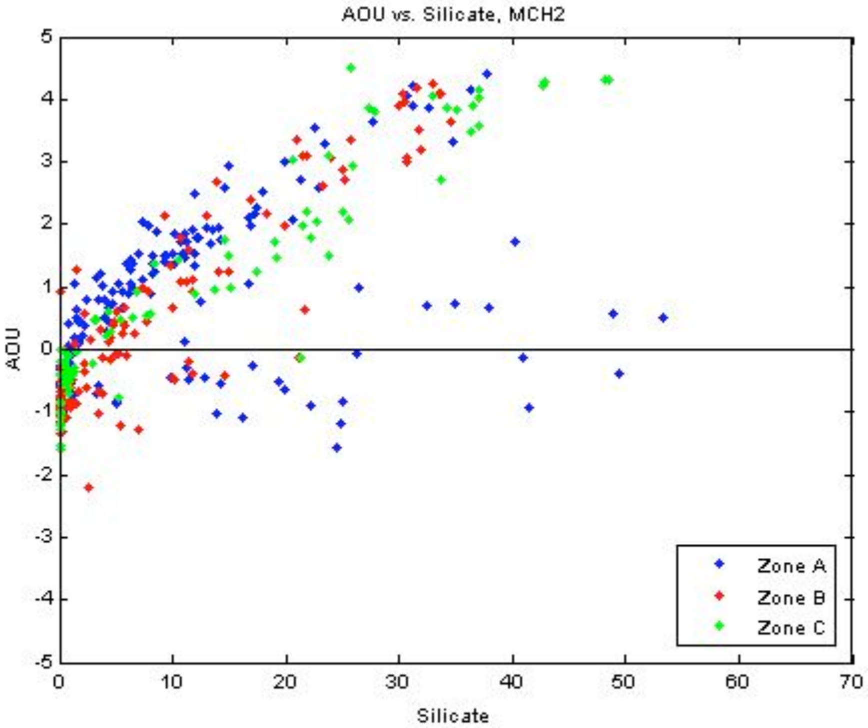

Figure 4.12. AOU (ml/l) vs. silicate (μM/l) concentrations during the June cruise, 2004. Blue, green, and red dots indicate measurements made at zones A, B, and C respectively.

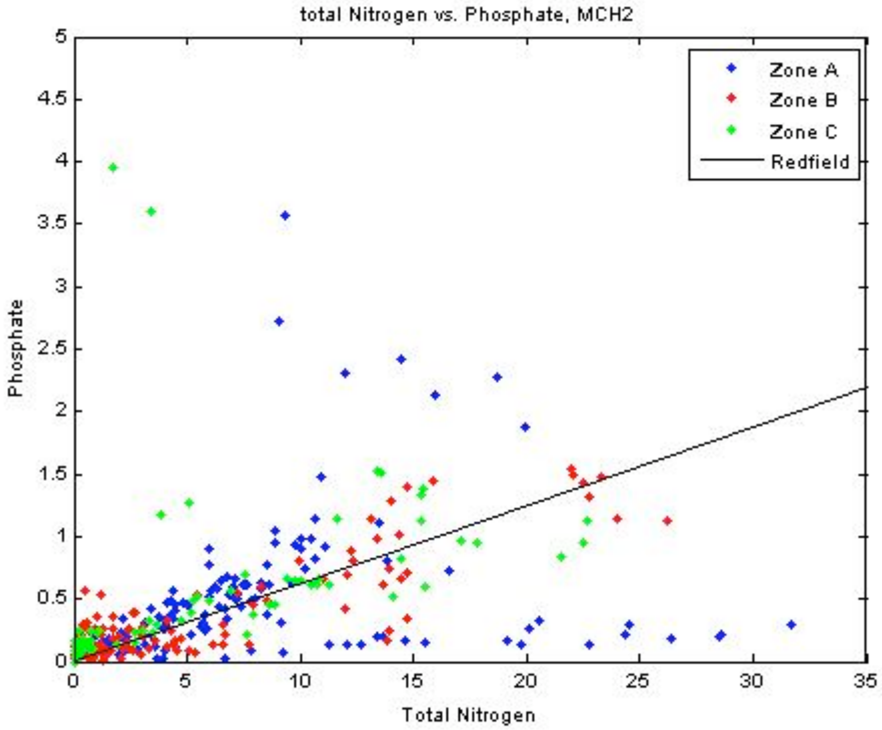

Figure 4.13. Total nitrogen (μM/l) vs. phosphate (μM/l) plot for June 2004 cruise. Color of dots indicate spatial region of data collection.

remineralization. Phosphate concentrations were small above the pycnocline but below the pycnocline high amounts were being remineralized, Figure 4.11. These unsaturated samples were hypoxic.

4.2.3. Correlations

As in the April cruise, all supersaturated waters (negative AOU) were excluded from correlation calculations to isolate processes occurring below the pycnocline. In general, correlations increased in June. During this cruise, oxygen was significantly correlated with all three nutrients. The nutrients were positively and significantly correlated with each other. This indicates that during peak hypoxia, nutrients were in abundance at the oxygen-depleted areas and were being remineralized below the pycnocline. All correlations are summarized in Table 4.4. When the correlations were separated into zone, many of the correlations improved, particularly in zone B (i.e., > 0.9). It is noteworthy that nitrate versus phosphate correlations decrease in zones A and C, i.e., those areas closest to the freshwater sources.

Figure 4.13 shows the relationship between total nitrogen and phosphate and its relation to the Redfield Ratio below the pycnocline for this cruise. The ratio of total nitrogen to phosphate was 17.41. Below the pycnocline the processes that affect the Redfield Ratio are regeneration and decay of organic matter. As with the April cruise, zone A is phosphate limited, as indicated by a high Redfield Ratio of 18.36. Zones B and C however, show less than Redfield Ratio total nitrogen to phosphate ratios of 13.64 and 13.11 respectively.

Table 4.4. Summary of correlations during the June 2004 cruise. Correlation coefficients in bold indicate significance at 95% level.

		Correlation Coefficient, R			
Property1	Property2	(All unsaturated points)	Zone A	Zone B	Zone C
Oxygen	Total Nitrogen	**-0.62**	-0.22	**-0.91**	**-0.60**
Oxygen	Phosphate	**-0.75**	**-0.81**	**-0.93**	**-0.68**
Oxygen	Silicate	**-0.85**	**-0.70**	**-0.90**	**-0.92**
Total Nitrogen	Phosphate	**0.41**	0.29	**0.89**	0.12
Total Nitrogen	Silicate	**0.71**	**0.44**	**0.91**	**0.50**
Phosphate	Silicate	**0.77**	**0.74**	**0.91**	**0.79**

4.3. August Cruise

4.3.1. Oceanographic Conditions

The third cruise was conducted from 19 – 26 August, 2004. Figure 4.14 shows the near real-time sea surface conditions in the Gulf of Mexico on August 22, 2004. Here the Loop Current is visible along with a cyclone on its north edge. These features did not directly affect the circulation of the study area on the Louisiana Shelf.

From the middle of July to the middle of August, there was a peak in discharge from the Mississippi River into the Gulf of Mexico. During this cruise, only patchy hypoxia was seen. 28 out of the 59 stations were hypoxic. Most of the hypoxic stations (especially in zones B and C) were offshore, (Figure 4.15). In zone A, however, all the inshore stations were hypoxic.

About a week prior to this cruise, winds changed from upwelling favorable to downwelling favorable, i.e., they were now seen to be coming from the east/southeast. They helped in breaking down the density stratification and injecting oxygen into the bottom layers. This process marked the beginning of dissipation of hypoxia on the Texas-Louisiana Shelf.

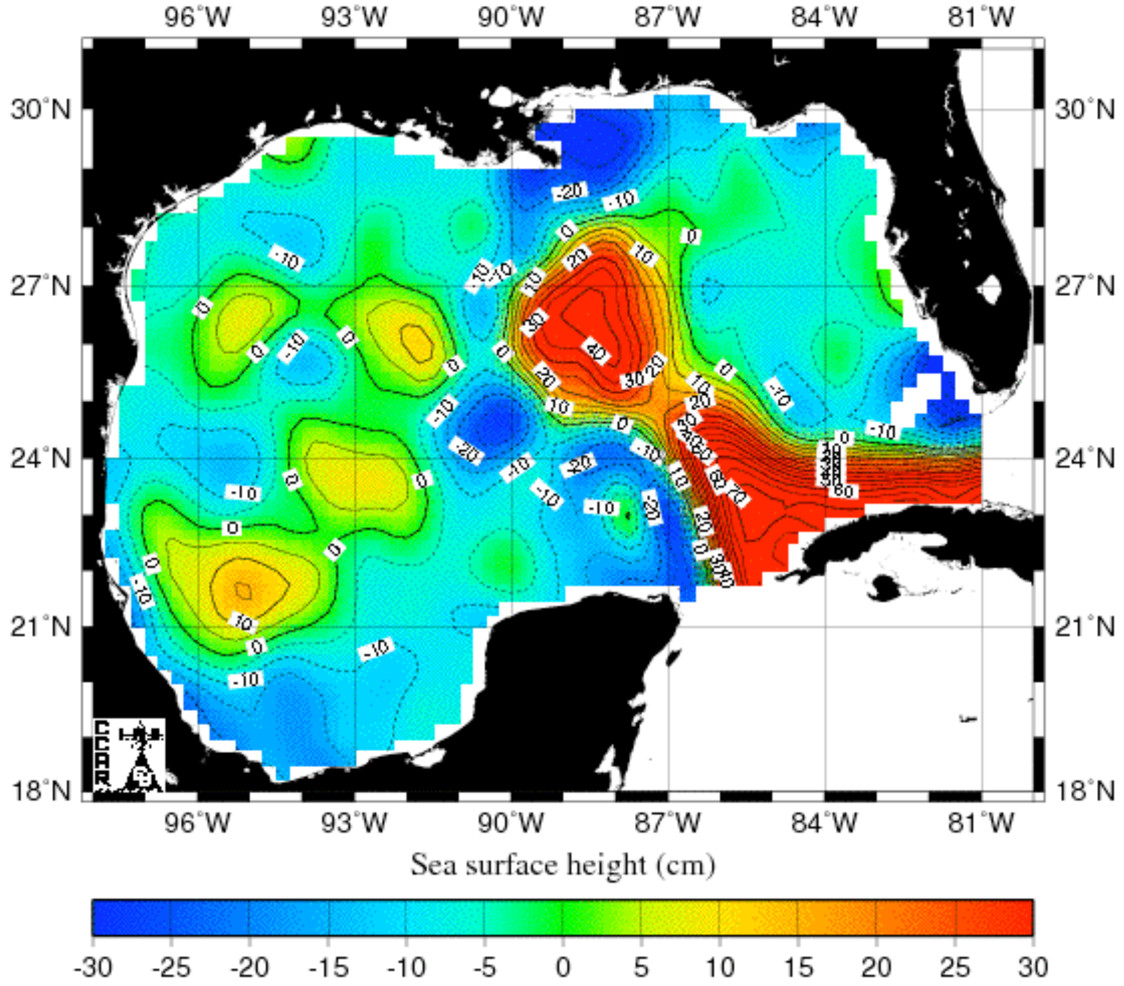

Figure 4.14. Sea surface height of the Gulf of Mexico on August 26, 2004. (Figure courtesy of Dr. R. Leben, Colorado Center for Astrodynamics Research, Dept. of Aerospace Engineering Sciences, University of Colorado). URL: ‘http://argo.colorado.edu /~real- time/gsfc_gom-real-time_ssh/’.

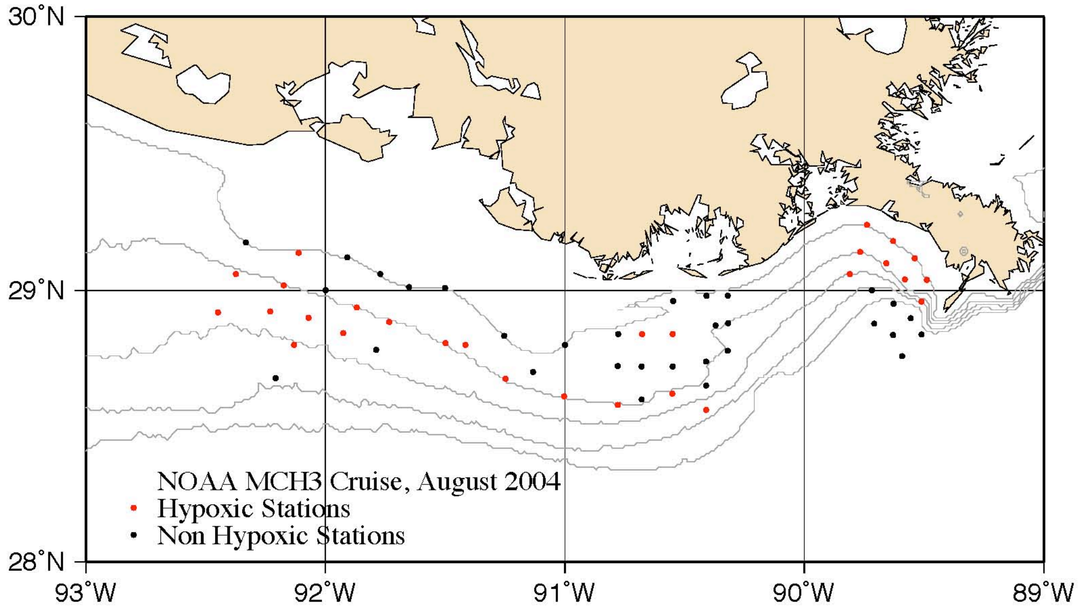

Figure 4.15. Summary of hypoxic stations during the August cruise in 2004. The red dots represent stations that were hypoxic while the black dots represent the non-hypoxic stations.

4.3.2. Property Distributions During August 2004

This cruise was unlike the other two cruises in terms of property distributions. Bottom hypoxia was observed at all the inshore stations in zone A, (Figure 4.16). In zone B two inshore stations were hypoxic; while in zone C, only one of the inshore stations was hypoxic. The rest of the hypoxic stations were offshore in zones B and C. Zone A was not hypoxic offshore of the 20 m isobath. As expected, surface oxygen concentrations were higher than bottom concentrations. Lowest oxygen concentrations were found in zone C. Bottom oxygen concentrations ranged between 0.165 ml/l to 4.92 ml/l. At the surface, the highest oxygen value was seen in zone A (9.421 ml/l). A few of the offshore stations in zone A were saturated with oxygen at the surface. Oxygen concentrations created a wave like structure that can be seen at the bottom (in zones B and C), with alternating high and low peaks in concentrations. This wave was also seen in the surface concentrations. Surface light transmission was low (25%) at the inshore stations of zone A (as would be expected due to river discharge) but higher (75%) at the offshore stations. In zones B and C, light transmission was high at the surface. At the bottom of the water column, transmission was low in zone B (20%), indicating resuspension of materials at the sediment-water column interface.

Salinity concentrations also displayed a similar wave like structure at both the surface and bottom. As expected, surface salinities were lower than bottom salinities. Lower salinities were seen at the mouths of the rivers and gradually decreased away offshore. Salinities concentrations ranged from 19.12 to 36.38. Lowest salinity was seen in zone A, off the mouth of the Mississippi River.

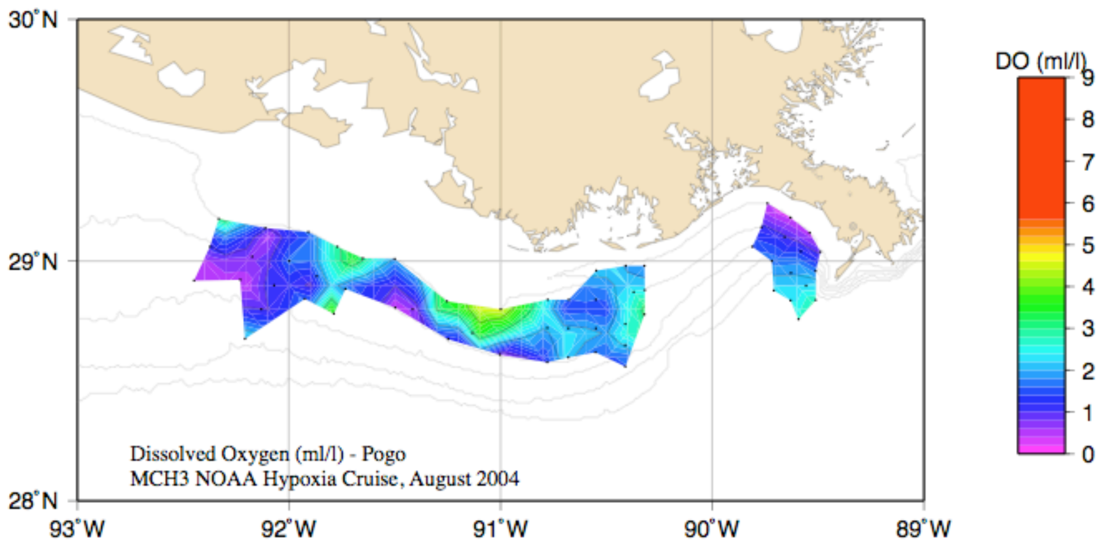

Figure 4.16. Bottom dissolved oxygen concentrations (ml/l) during the August cruise (MCH3), August 19 to August 26, 2004. Bathymetric contours shown are 10, 20, 30, 40 and 50 m isobaths.

Nitrate concentrations were extremely low in the surface waters in all three zones during this cruise. At the bottom, however, high concentrations of nitrate were found in all three zones, with the highest value being in zone A at an offshore station (13.3 μM/l). The inshore stations of zone B did not have high concentrations at either the surface or the bottom, but high concentrations were seen at offshore stations in zone B. Between zones B and C and zone C, high concentrations of nitrate were seen. High concentrations of ammonium, which are a product of regeneration, were also seen at the bottom, with maximum concentration of 11.91 μM/l.

Table 4.5. Basic statistics of nutrient values during the August 2004 cruise. bd = below detection.

Nutrient	Maximum (μM/l) / (Zone)	Minimum (μM/l)	Mean (μM/l)
Total Nitrogen	16.68 / (C)	bd	1.97
Nitrate	12.58 / (B)	bd	1.55
Phosphate	2.66 / (A)	bd	0.30
Silicate	76.83 / (C)	bd	8.63

Phosphate and Silicate are highly correlated during this cruise, with very low concentrations at the surface, but higher concentrations at the bottom in all three zones. Highest phosphate concentrations were seen in the zone A, while highest silicate concentrations were seen in zone C, both at offshore stations. Low phosphate concentrations in the surface waters was due to the uptake by phytoplankton, while diatoms consumed silicate. The presence of high concentrations of these two nutrients at the bottom of the water column is indicative of remineralization. In case of all three nutrients, the wave like structure was observed in the bottom water concentrations. The range of all nutrients is summarized in Table 4.5. Note that bulk mean concentrations were lowest for the August cruise. this is likely the result of the low nutrient loading conditions for this time of the year.

In Figures 4.17, 4.18 and 4.19, we see the relationship between oxygen and nutrients. The principal difference between this set of figures and the April and June set of figures, is that the river signature is not present as supersaturated waters (large negative AOU) and high nutrients. However, high nutrients are seen in extremely unsaturated waters (large positive AOU), which show the occurrence of hypoxia. Total nitrogen is the dominant nutrient in zone A. Silicate is dominant in zone C. Phosphate is present in small amounts in all three zones.

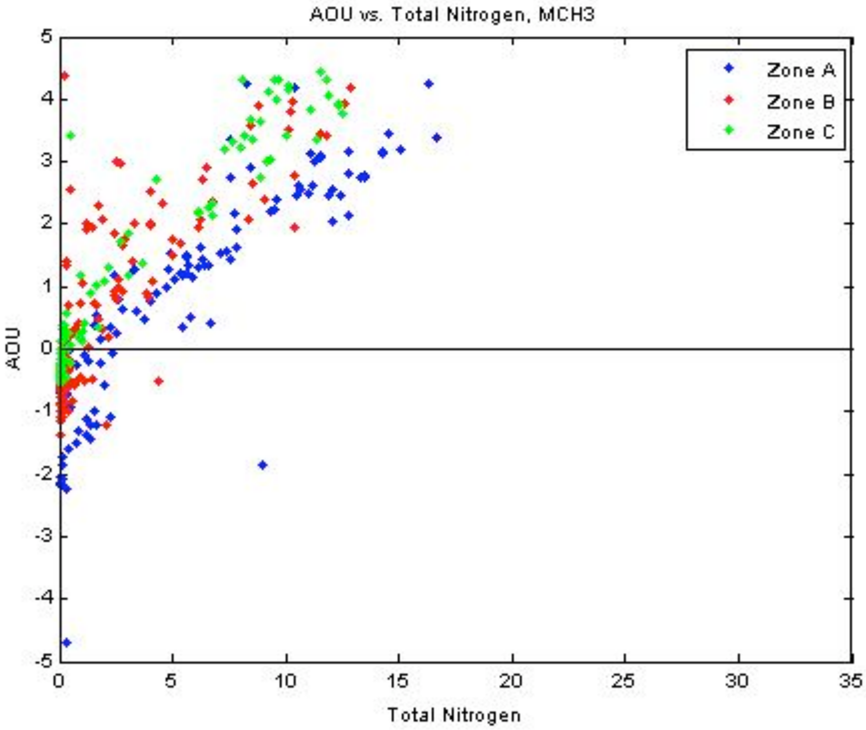

Figure 4.17. AOU (ml/l) vs. total nitrogen (μM/l) concentrations during the August cruise, 2004. Blue, green, and red dots indicate measurements made at zones A, B, and C respectively.

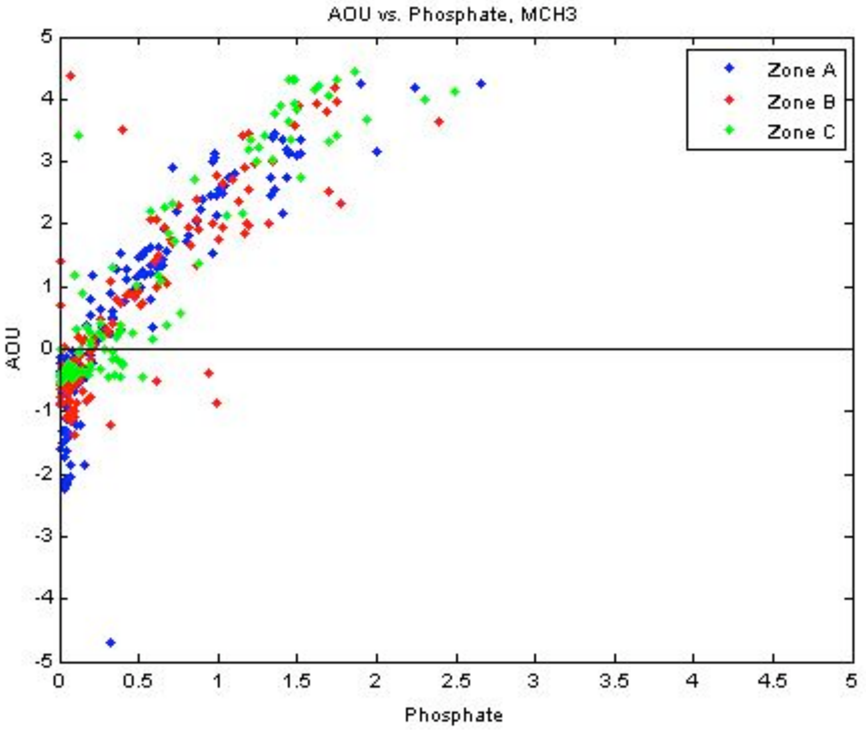

Figure 4.18. AOU (ml/l) vs. phosphate (μM/l) concentrations during the August cruise, 2004. Blue, green, and red dots indicate measurements made at zones A, B, and C respectively.

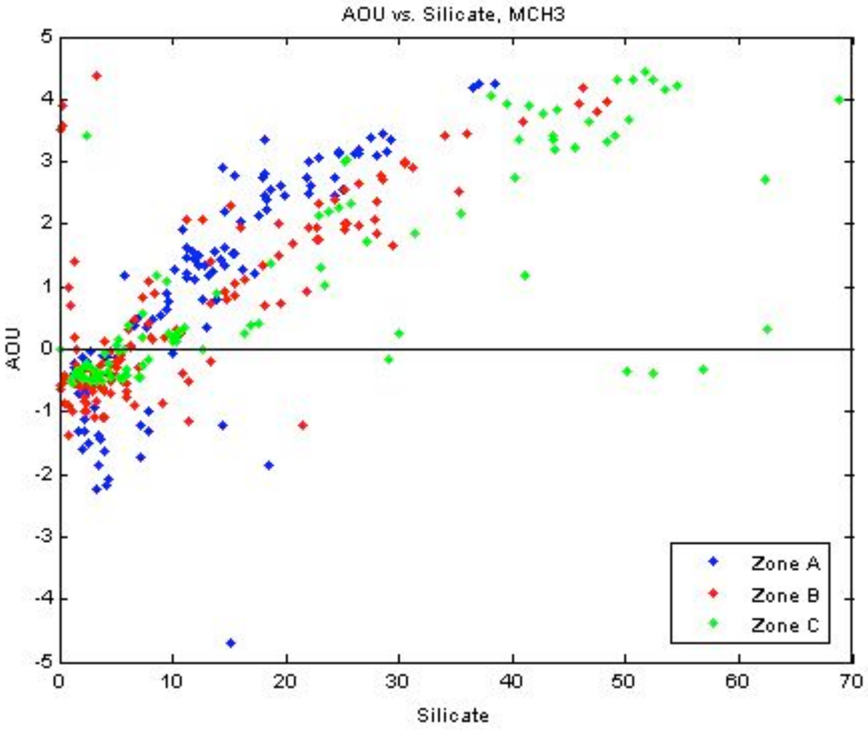

Figure 4.19. AOU (ml/l) vs. silicate (μM/l) concentrations during the August cruise, 2004. Blue, green, and red dots indicate measurements made at zones A, B, and C respectively.

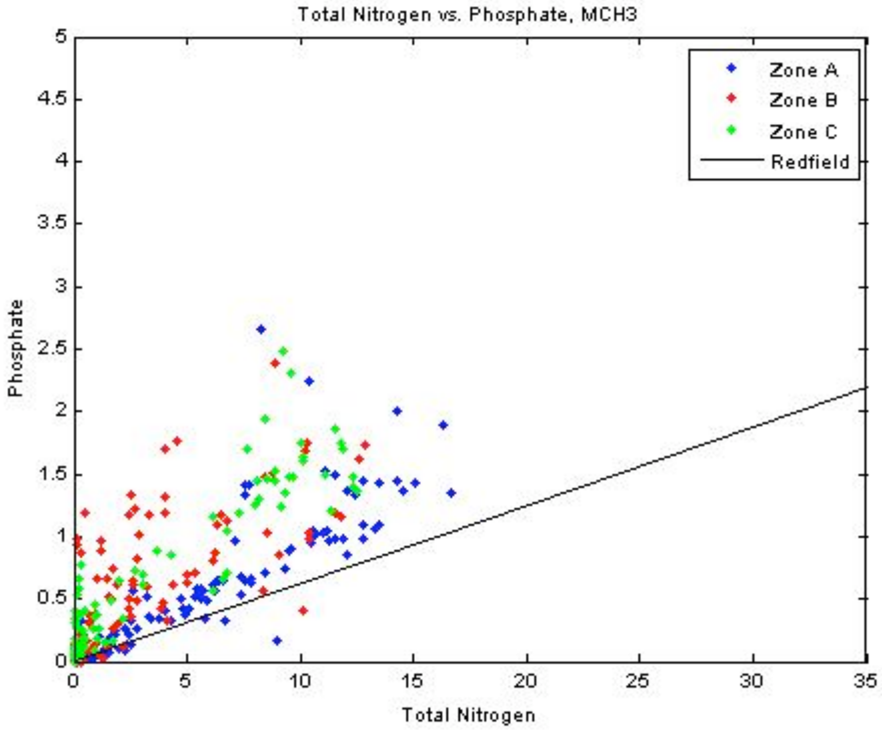

Figure 4.20. Total nitrogen (μM/l) vs. phosphate (μM/l) plot for August 2004 cruise. Color of dots indicate spatial region of data collection.

Table 4.6. Summary of correlations during the August 2004 cruise. Correlation coefficients in bold indicate significant correlation at 95% level.

		Correlation Coefficient, R			
Property1	Property2	(All unsaturated points)	Zone A	Zone B	Zone C
Oxygen	Total Nitrogen	**-0.72**	**-0.89**	**-0.71**	**-0.93**
Oxygen	Phosphate	**-0.84**	**-0.90**	**-0.77**	**-0.89**
Oxygen	Silicate	**-0.71**	**-0.91**	**-0.59**	**-0.78**
Total nitrogen	Phosphate	**0.59**	**0.75**	**0.64**	**0.90**
Total Nitrogen	Silicate	**0.48**	**0.76**	**0.55**	**0.74**
Phosphate	Silicate	**0.74**	**0.93**	**0.78**	**0.77**

4.3.3. Correlations

The correlation coefficients for this cruise (for all unsaturated points) are summarized in Table 4.6, the bold correlations representing significance at 95% level. All the nutrients were negatively correlated with oxygen and all the correlations were high and significant at 95% level. In general, correlations are the highest of all three cruises and all are significant. The best correlations between oxygen and nutrients occurred in zone C. Nutrients were positively correlated with one another. All nutrients were remineralized below the pycnocline. As we have seen earlier, hypoxic areas were hot spots of remineralization at the bottom of the water column and near the sediments.

Figure 4.20 summarizes the total nitrogen to phosphate ratio and its relation to the Redfield Ratio. The system is nitrate limited, especially above the pycnocline. In all three zones, the ratio of total nitrogen to phosphate is less than the Redfield Ratio below the pycnocline. There were no phosphate limited samples during the August cruise.

4.4. Hypothesis Testing

In this thesis, I tested one hypothesis and in this section I present a discussion of the findings related to the hypothesis.

I determined that bottom dissolved oxygen was inversely correlated with bottom dissolved nutrients (nitrate, phosphate and silicate) during April, June and August 2004 cruises in all three zones. However, the magnitude of the correlations varied seasonally with each cruise, and also spatially depending upon the structure of hypoxia and the physical processes controlling stratification.

CHAPTER V

SUMMARY AND CONCLUSIONS

In this chapter, I present a summary of the major findings of the three cruises presented previously. As discussed in Chapter II, the process zones hypothesized by Rowe and Chapman [2002] are not particularly tied to any geographical region and one or more processes zone may occur at a specific location depending on the physical and biochemical conditions taking place there. Using auxiliary data such as light transmission and chlorophyll-a concentration taken from sensors on the CTD package, I assign the process zones to geographical locations on the shelf to identify the spatial distribution of the zones and how the zones evolved during the hypoxic season of 2004. By so doing, a climatology or frequency of occurrence of process zones can be constructed using multiple cruises during the year, to identify those processes that tend to dominate a given area. Such a distribution would complement the frequency of occurrence of hypoxia maps produced by Rabalais et al. [2002a] and could assist coastal managers to better identify regions likely to become hypoxic in a given year under a more specific set of oceanographic conditions. Also additional nutrient data such as ammonium concentration is used to provide evidence that high nitrate, phosphate, and silicate concentrations are the result of remineralization processes beneath the pycnocline and not due to direct nutrient input in the surface freshwater river plume. Other cruises not discussed in this thesis have shown that nutrient-rich subpycnocline waters may not be light-limited and may fuel primary production (S. DiMarco, personal communication). When accompanied by cross-shelf advection, this may represent a mechanism to transport organic material across the shelf and may contribute to additional respiration and oxygen depletion far from the regions directly influenced by the freshwater plume.

5.1. April Cruise Summary

During the April cruise, no hypoxia was observed on the Louisiana Shelf. Dissolved oxygen concentrations were below saturation beneath the pycnocline but not hypoxic across the study region. Surface waters were supersaturated reflecting the presence of the river plume. Dissolved oxygen concentrations were highest inshore, and decreased towards the offshore stations. Nutrients were highest at the surface in zone A reflecting the presence of freshwater input from the Mississippi River. Elevated nutrients were also found south of Atchafalaya Bay. Phosphate concentrations showed similar spatial distribution to that of nitrate. Nitrate to phosphate ratios were highest (40.21) at inshore stations closest to the Mississippi River indicating possible phosphate limitation. Transmission at the surface was low (about 40%) due to an abundance of particulate material in the freshwater plume.

During this cruise, dissolved oxygen concentration was negatively and significantly correlated with total nitrogen and silicate, but negatively and non-significantly correlated with phosphate. High negative correlations between oxygen and nitrate and silicate were seen in zone A where there was high nutrient (nitrate and silicate) concentrations discharged by the Mississippi River. Phosphate was the limiting nutrient with very low concentrations leading to low non-significant correlation with oxygen. In zones B and C, there were more complicated biochemical processes that offered variability in the magnitude of the correlations. Nutrients were positively and significantly correlated with each other. High positive correlations were seen in zone A due to the proximity to the river source. In zones B and C, correlations were not high due to various biological processes, including respiration and regeneration.

5.2. June Cruise Summary

The June cruise witnessed extensive hypoxia on the Louisiana Shelf at almost all inshore stations between the Mississippi delta and 93°W. A few of the offshore stations were also hypoxia particularly near the 20 m isobath in between zones B and C. Density stratification was strong at the inshore stations of zones C and between zones B and C and very light winds discouraged mixing. Nutrient concentrations were highest closest to the Mississippi River in zone A. At the surface, concentrations were lower than at the bottom. Remineralization of all three nutrients was taking place at the bottom of the water column based on an analysis of high ammonium concentrations at the bottom. Near-bottom in zone B, low light transmission values (order of 20%) likely was the result of resuspension of bottom particulate matter as surface water were clear.

During this cruise, below the pycnocline dissolved oxygen was negatively and significantly correlated with nutrient concentrations, likely as a result of respiration and the remineralization of nitrate and other nutrients. Highest negative correlations were seen in zone B where most of the remineralization was taking place, indicated by high ammonium concentrations. The nutrients were positively and significantly correlated with each other especially below the pycnocline where high amounts of nutrients were being remineralized.

5.3. August Cruise Summary

In August, there was patchy hypoxia on the Louisiana Shelf. Most of the offshore stations were hypoxic but only a few of the inshore ones hypoxic. Nutrients were very low at the surface waters but present in high amounts at the bottom, indicating that remineralization was taking place at the bottom.

In August, nutrients (nitrate, phosphate, silicate) below the pycnocline were negatively and significantly correlated with oxygen. High negative correlations were seen in all the three zones. Also all the nutrients were positively and significantly correlated with each other in all the three zones. This indicated that high nutrients were seen at regions of low oxygen concentrations, i.e., during peak hypoxia all three nutrients were being remineralized at the bottom of the water column.

In all the three cruises, surface oxygen was higher than bottom oxygen in all the three zones. Salinities were lower at the surface and higher at the bottom for all the three cruises. Nutrient concentrations were generally higher in the surface waters. But in August, this situation was drastically reversed when the surface was completely devoid of nutrients, but remineralization was injecting new nutrients into the bottom waters.

Considering the property distributions and looking at additional information such as light transmission and fluorescence on the Louisiana Shelf, the MCH zones may be correlated to the RC02 zones, Figures 5.1, 5.2 and 5.3. During the first cruise, the Brown zone was formed at the mouth of the Mississippi and Atchafalaya Rivers, at the inshore stations of MCH zones A and C, Figure 5.1. These regions were characterized by high surface oxygen and nutrients. Light penetration was low at the surface due to the presence of high volume of particulates brought down by the rivers. Fluorescence was also low at the surface, indicating an absence of production. The Green zone was found adjacent to the Brown zone and was made up of the offshore stations in zones A and C. Here surface nutrients were high, i.e., above 30 μM/l, although not as high as that found in the brown zone, which were typically about 20 μM/l. Light penetration was high at the surface, 65%, and low at the bottom, 35%, due to settling of particulate material. Fluorescence indicating chlorophyll-a concentration was large, while AOU values were large and negative at the surface, indicating photosynthesis likely as a result of a phytoplankton bloom. The Blue zone is identified with the MCH zone B, having very low nutrients at the surface and higher nutrients at the bottom, indicating remineralization processes occurring beneath the pycnocline.

In the second cruise, the Brown zone included the inshore stations of zone A, Figure 5.2. Here nutrients were high at the surface. Light penetration was low at the surface, about 25%, as was fluorescence. The Green zone coincided with a region north of the 20 m isobath in MCH zone B. The Green zone had high production in the surface waters indicated by high fluorescence. Light penetration was high at the surface (65%) and gradually diminished at the bottom to 25%. During this cruise there were two blue zones – one in MCH zone BC, i.e., the region in between actual zones B and C, and the

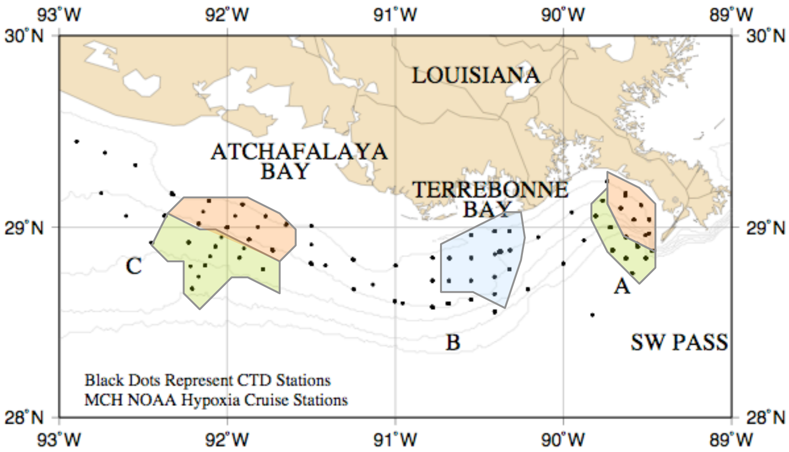

Figure 5.1. Schematic of Rowe and Chapman zones formed during the April 2004 cruise. Areas shaded in brown, green and blue represent the Brown, Green and Blue zones respectively.

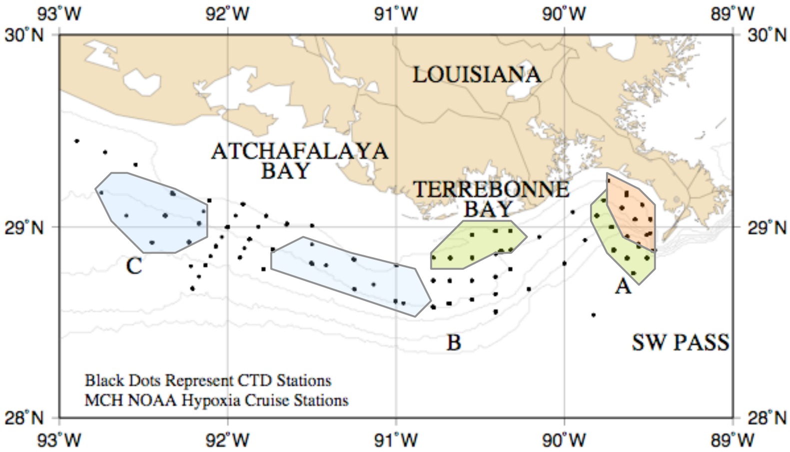

Figure 5.2. Schematic of Rowe and Chapman zones formed during the June 2004 cruise. Areas shaded in brown, green and blue represent the Brown, Green and Blue zones respectively.

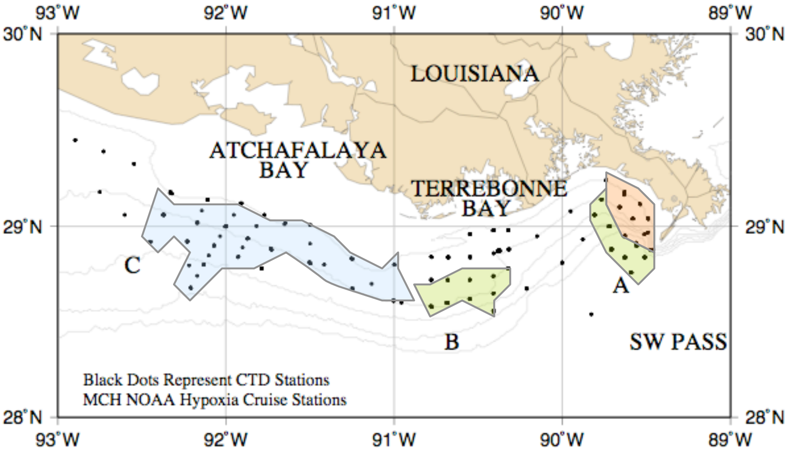

Figure 5.3. Schematic of Rowe and Chapman zones formed during the August 2004 cruise. Areas shaded in brown, green and blue represent the Brown, Green and Blue zones respectively.

other one in the western part of MCH zone C. Both these regions had very low nutrients at the surface, but high nutrients at the bottom, indicating remineralization in situ at the sediments. High concentrations of ammonium were also found at the bottom here, corroborating the process of remineralization.

In the third cruise, a situation similar to the previous two cruises was seen in zone A, where the inshore stations showed properties of the Brown zone and the offshore stations showed properties of the Green zone, Figure 5.3. In the Brown zone, nutrients were highest and light transmission was lowest at the surface, 40%. The Green zone was shifted offshore from the June cruise much like hypoxia and was formed at the offshore stations of zone B. There were very low nutrients at the surface (most of the nutrients being consumed by phytoplankton). Light penetration was high at the surface (80%) and decreased below the euphotic zone to about 20% at the bottom. The Blue zone was spatially the largest. It comprised of all the stations from the western edge of zone B all the way to the western edge of zone C. In this region surface nutrients were very low but there were high concentrations at the bottom, where remineralization was taking place. High concentrations of ammonium were found at the bottom, which also supported the process of remineralization.

The spatial cross-shelf scales on the LS are on the order of about 15-20 km [*Li et al.*, 1996]. In order to produce frequency of occurrence maps of the RC02 zones on the shelf, it is important to measure at small spatial scales, preferably on the order of 10 km. It would be easy to overlook the variance associated with small-scale processes while measuring at larger spatial scales. Furthermore, it would be useful to have long-term time-series data of oxygen, salinity, and nutrients to observe trends and resolve processes changing almost daily on the LS. Therefore, future efforts to quantify the processes affecting the timing and structure of hypoxia should be grounded in the knowledge of the temporal and spatial scales of the physical-biogeochemical processes that occur on the shelf, [*Hetland and DiMarco*, 2007].

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APPENDIX A

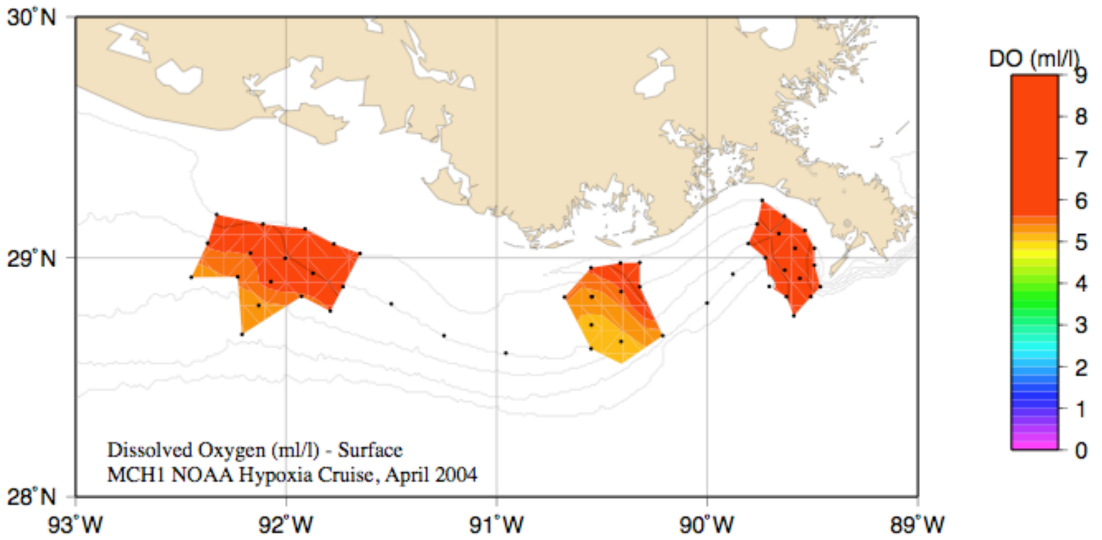

Figure A1. Surface plan view map of oxygen – April

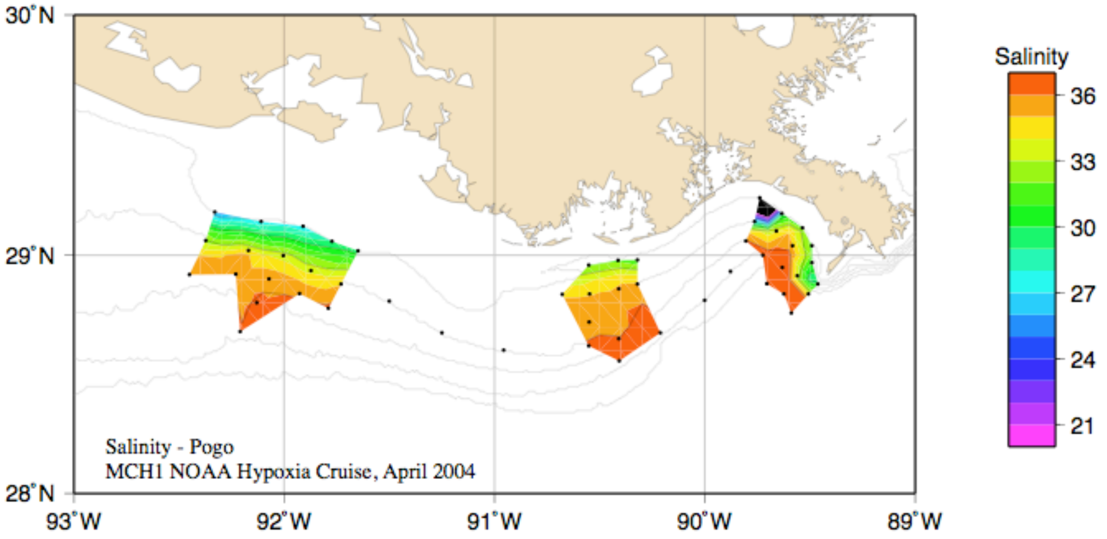

Figure A2. Bottom plan view map of salinity – April

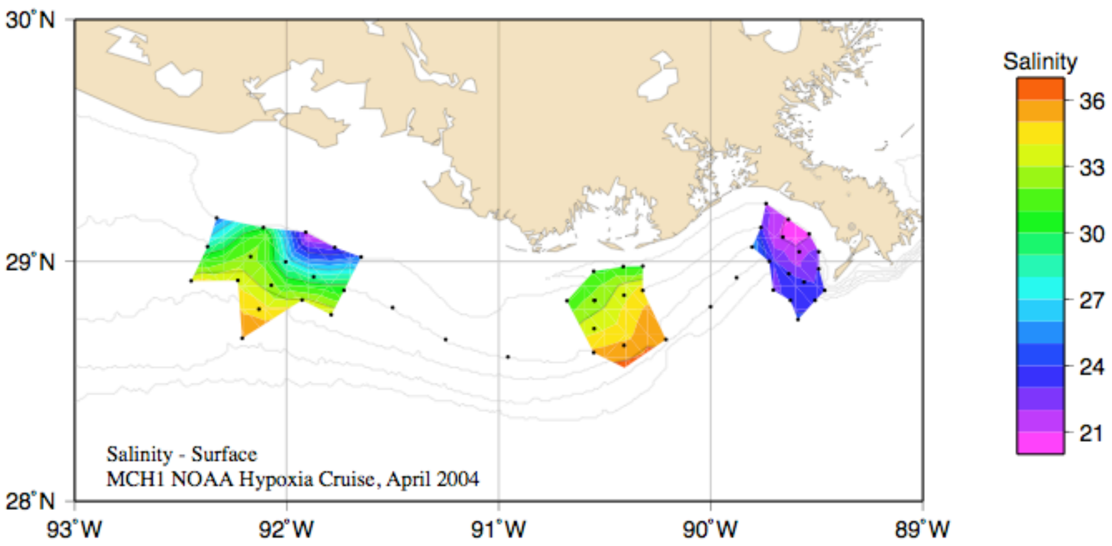

Figure A3. Surface plan view map of salinity – April

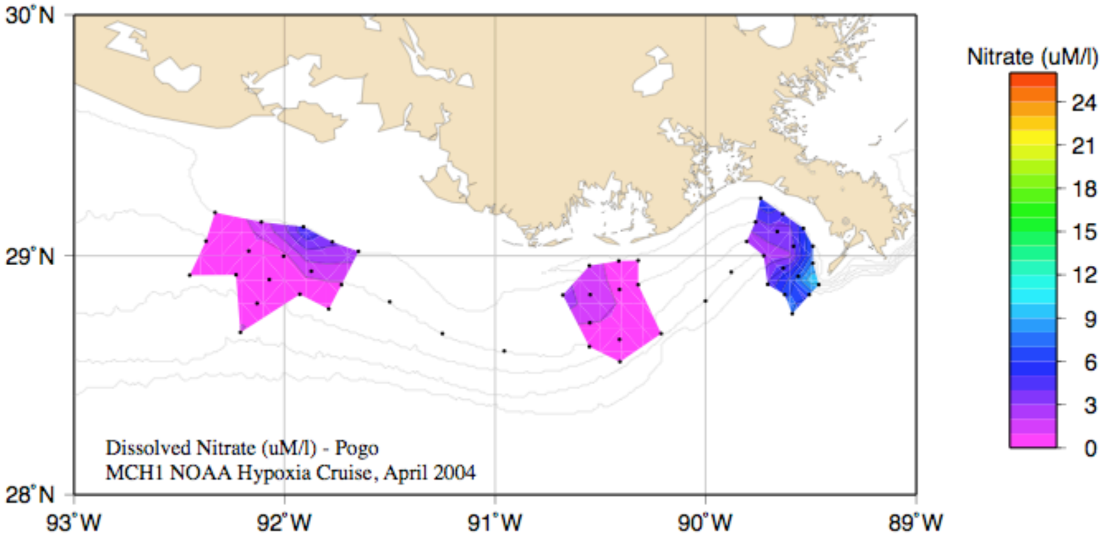

Figure A4. Bottom plan view map of nitrate – April

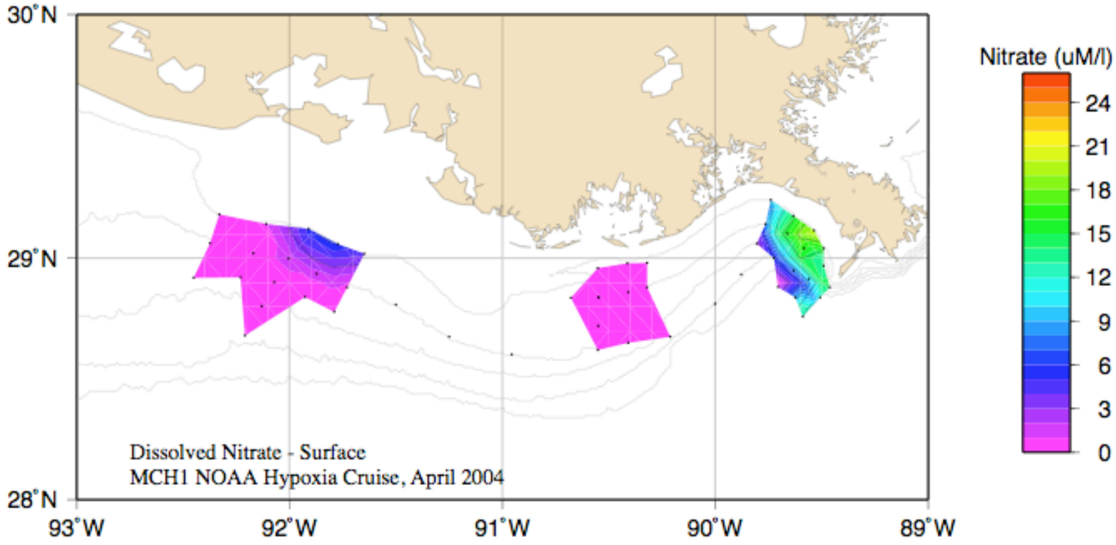

Figure A5. Surface plan view map of nitrate – April

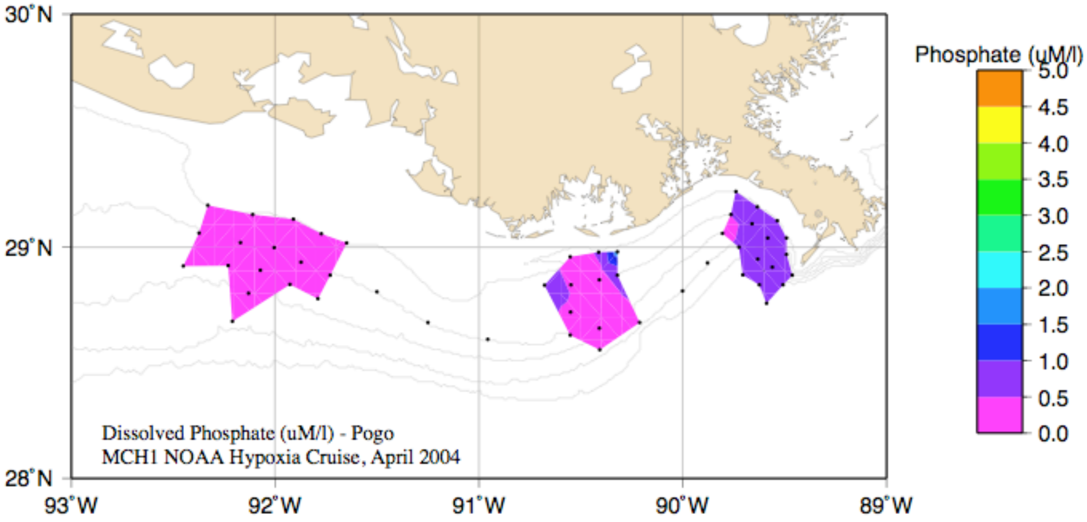

Figure A6. Bottom plan view map of phosphate – April

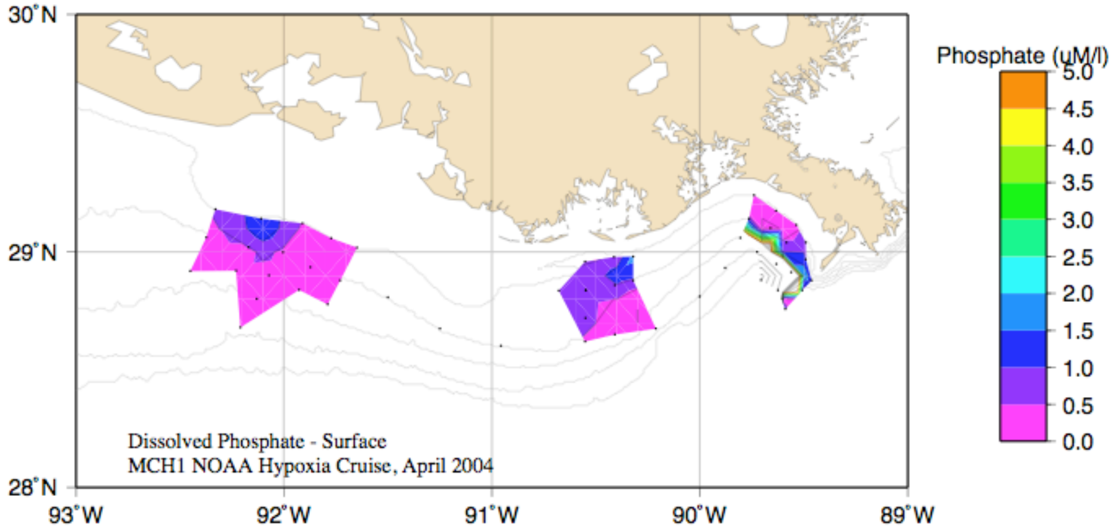

Figure A7. Surface plan view map of phosphate – April

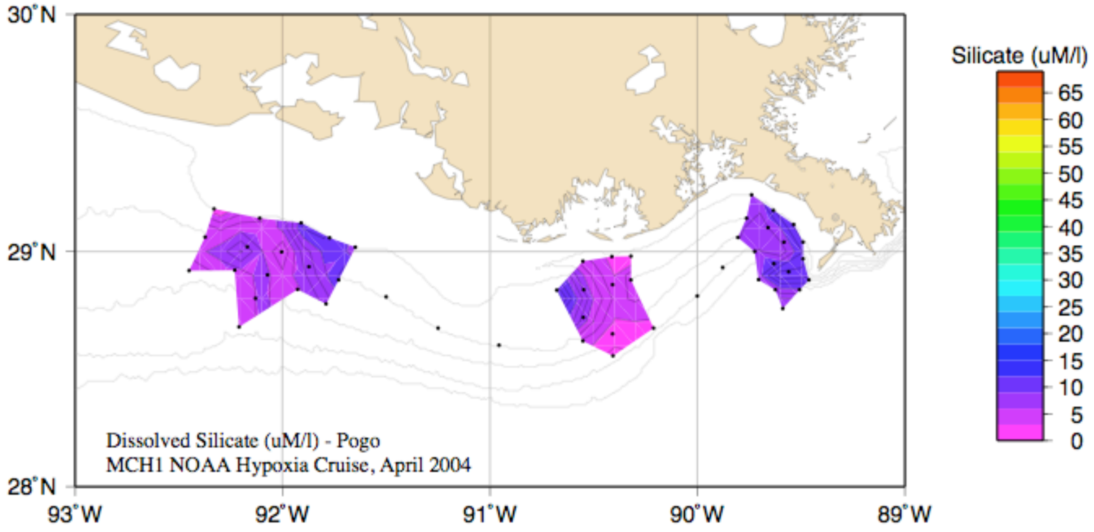

Figure A8. Bottom plan view map of silicate – April

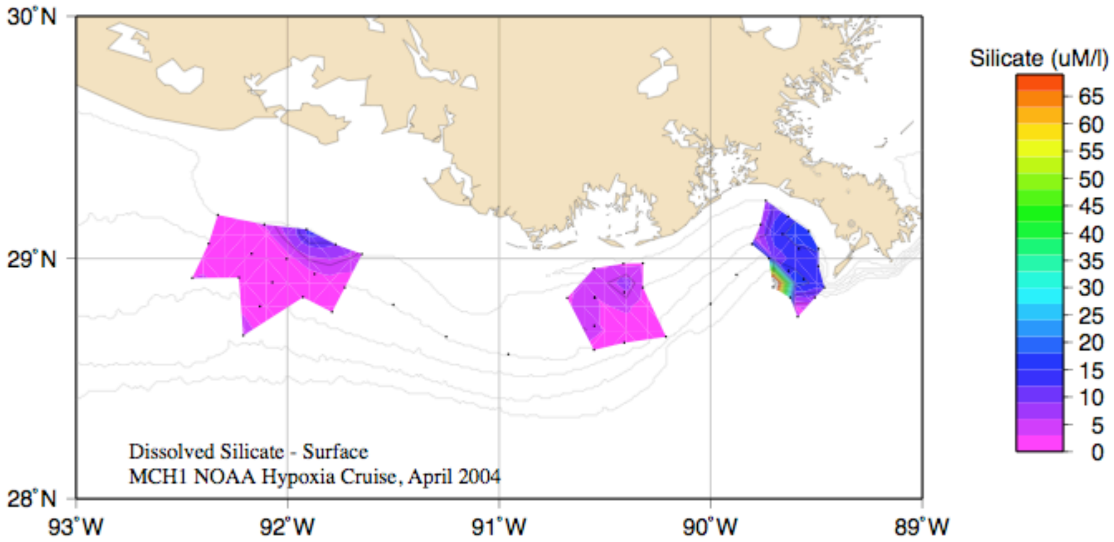

Figure A9. Surface plan view map of silicate – April

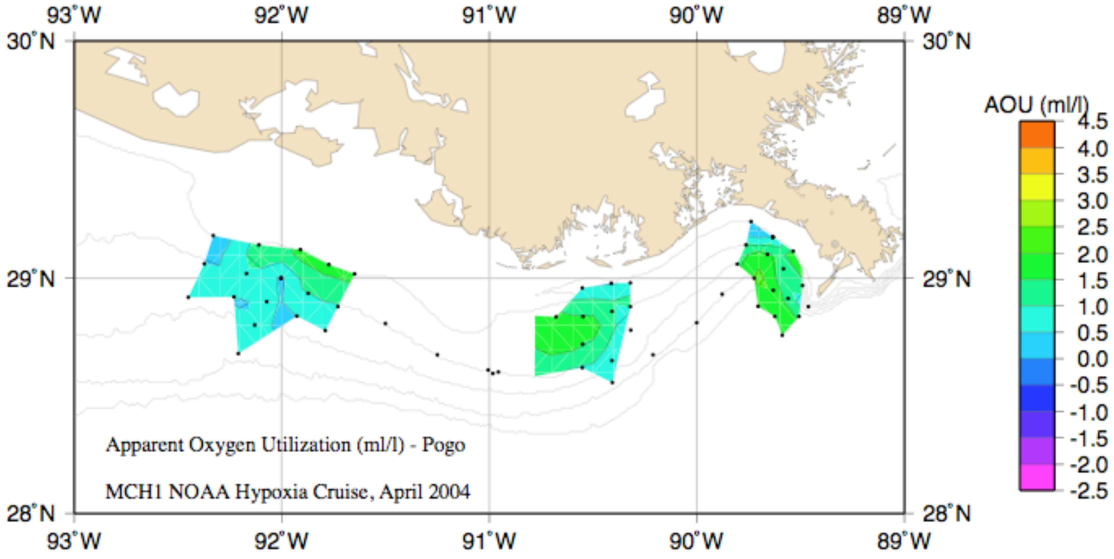

Figure A10. Bottom plan view map of Apparent Oxygen Utilization (AOU) - April.

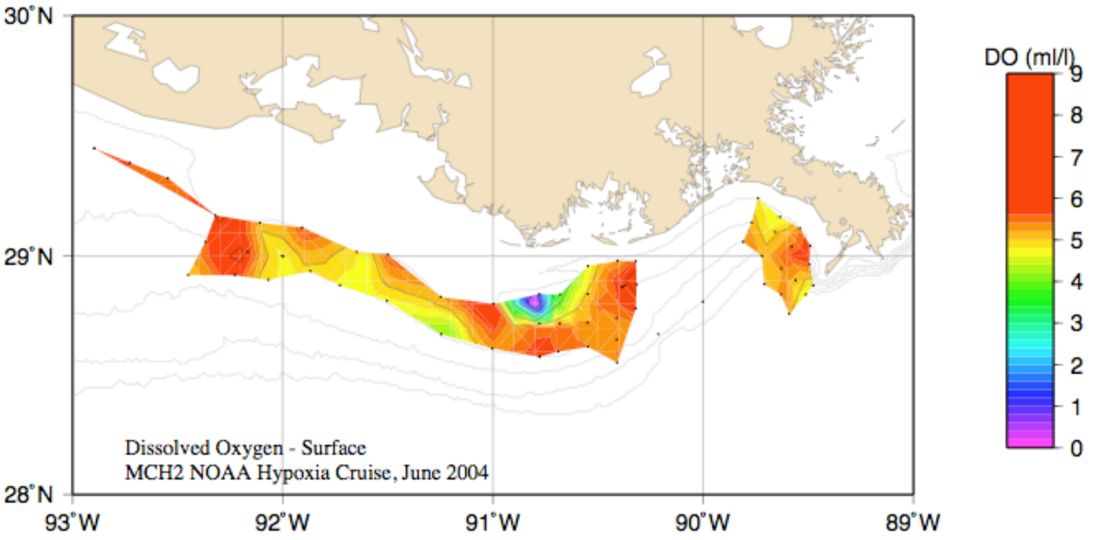

Figure A12. Surface plan view map of oxygen – June

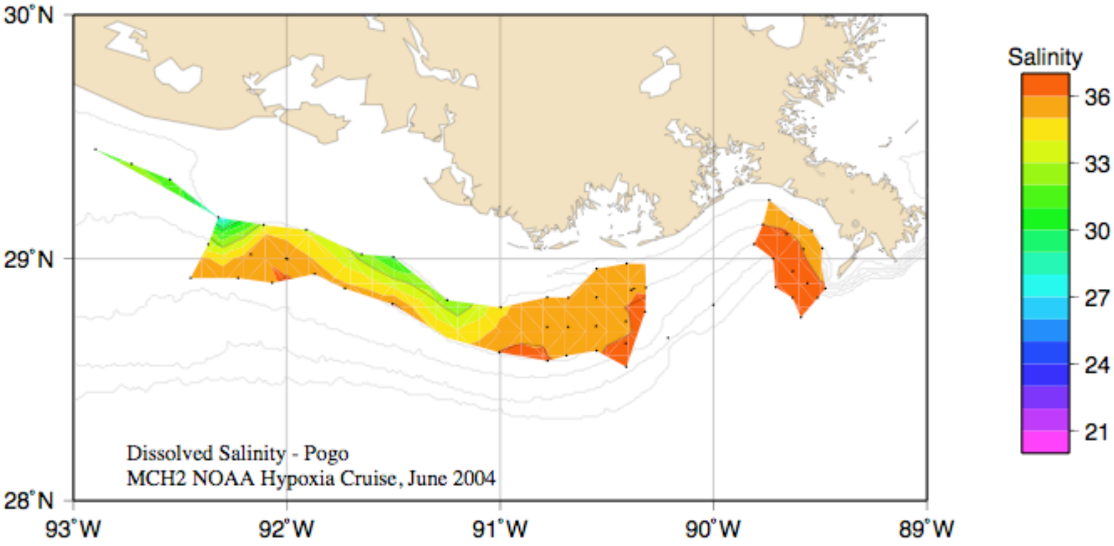

Figure A13. Bottom plan view map of salinity – June

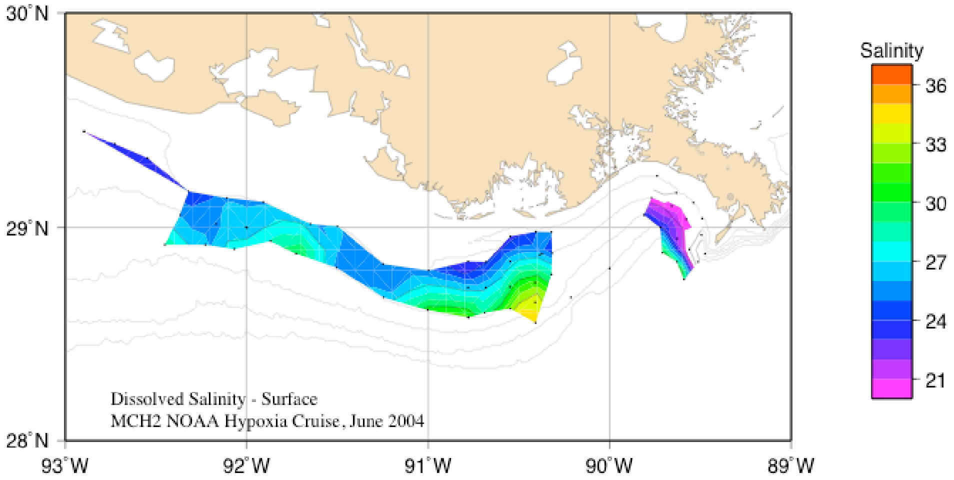

Figure A14. Surface plan view map of salinity – June

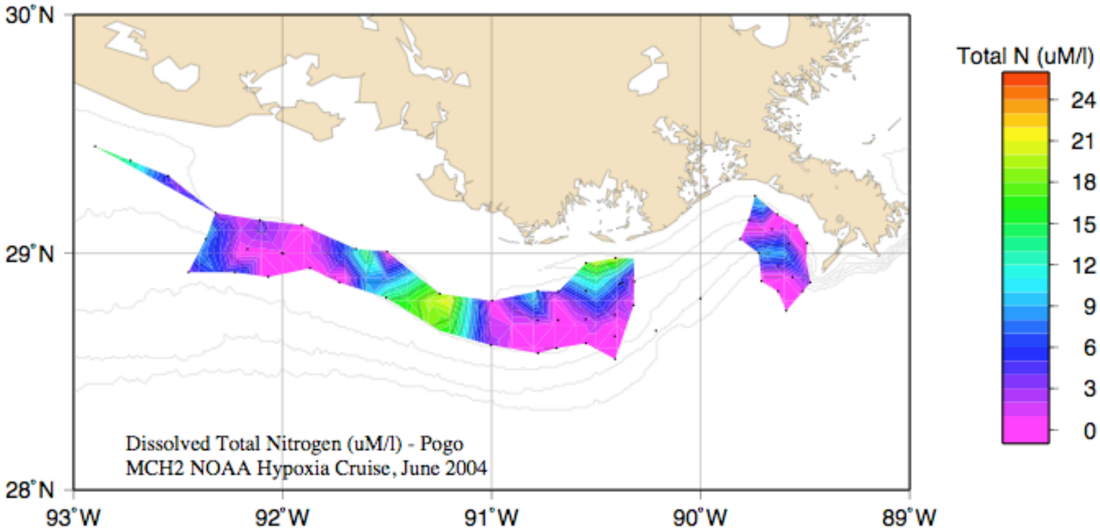

Figure A15. Bottom plan view map of total nitrogen – June

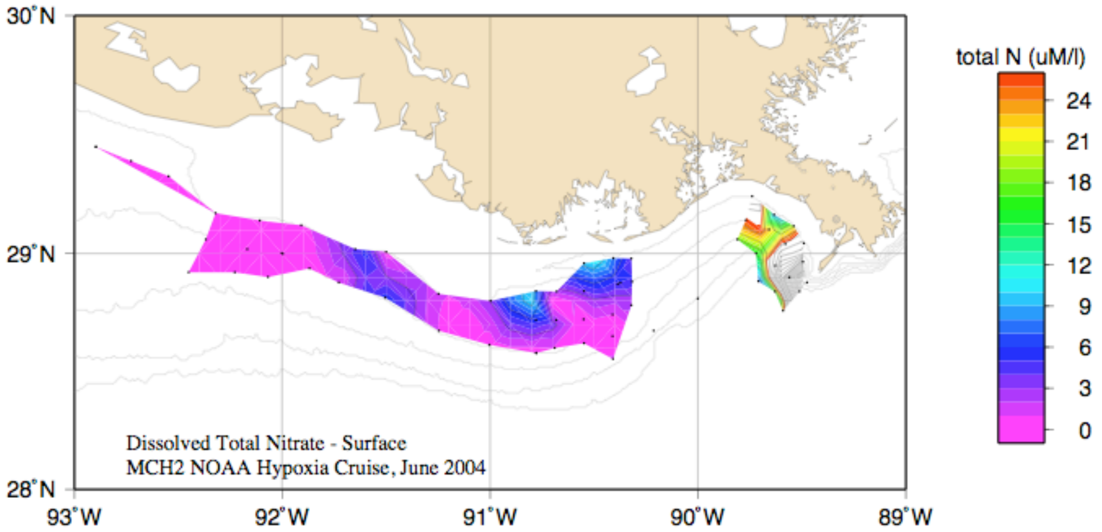

Figure A16. Surface plan view map of total nitrogen – June

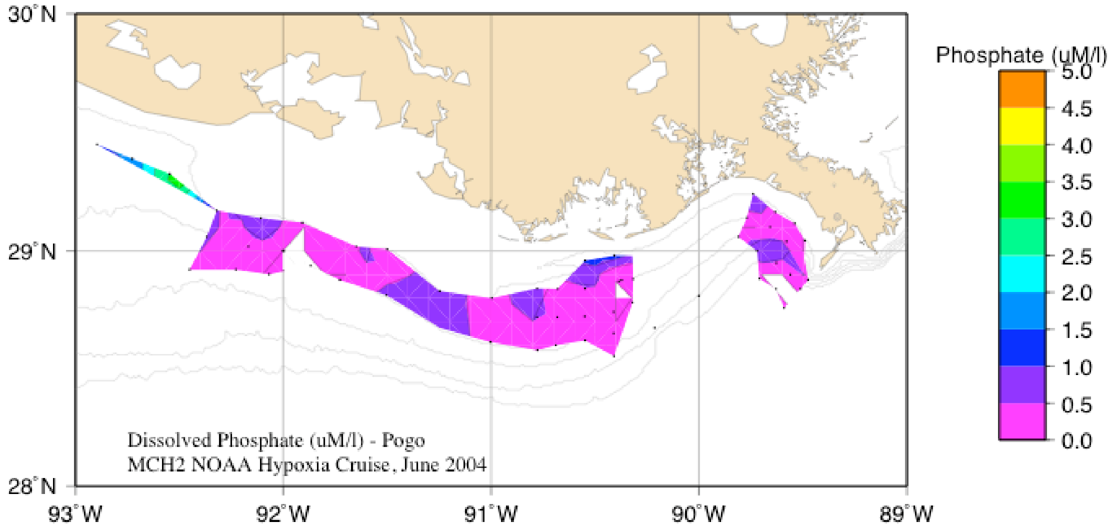

Figure A17. Bottom plan view map of phosphate – June

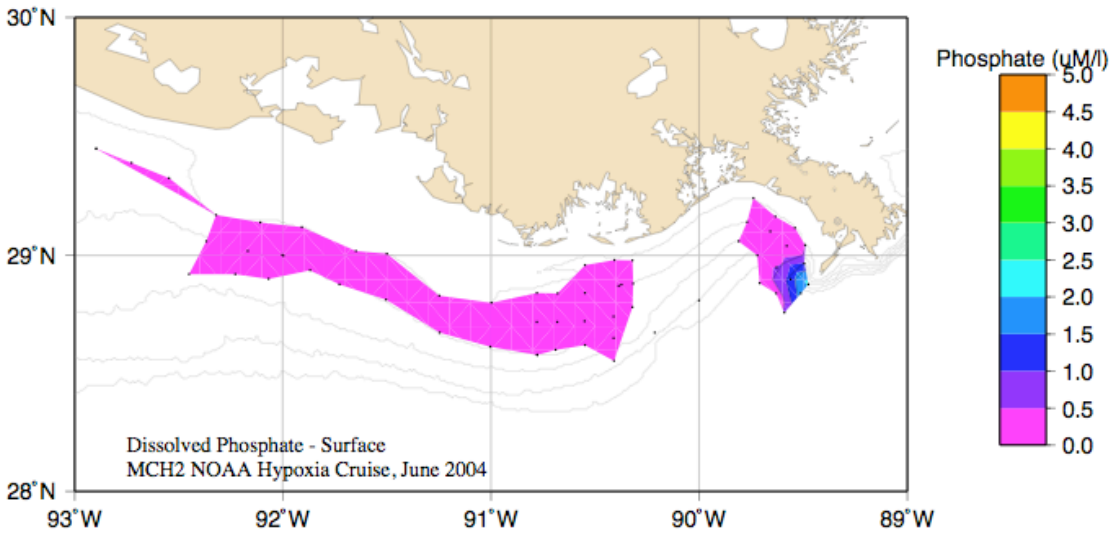

Figure A18. Surface plan view map of phosphate – June

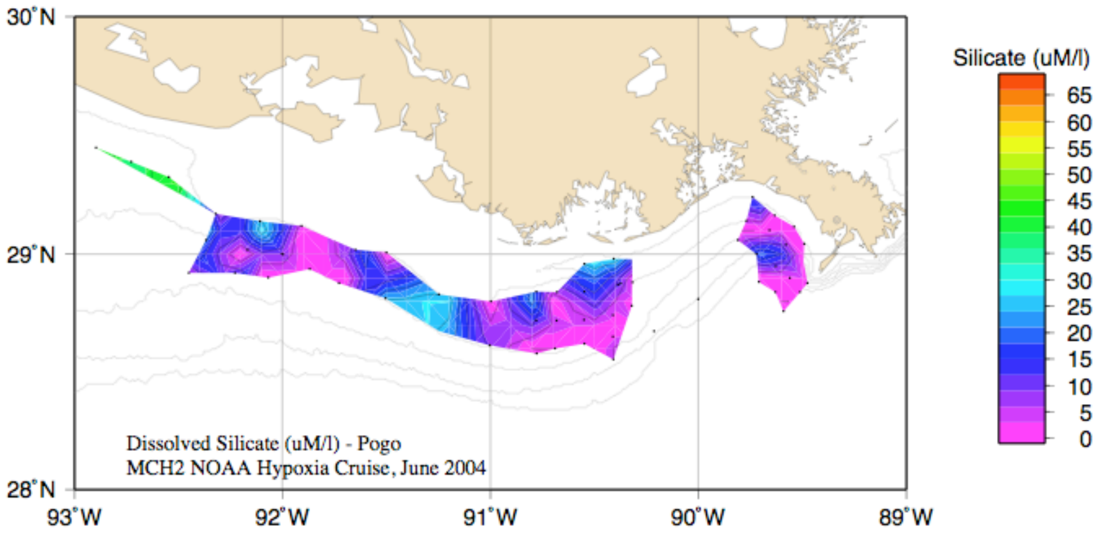

Figure A19. Bottom plan view map of silicate – June

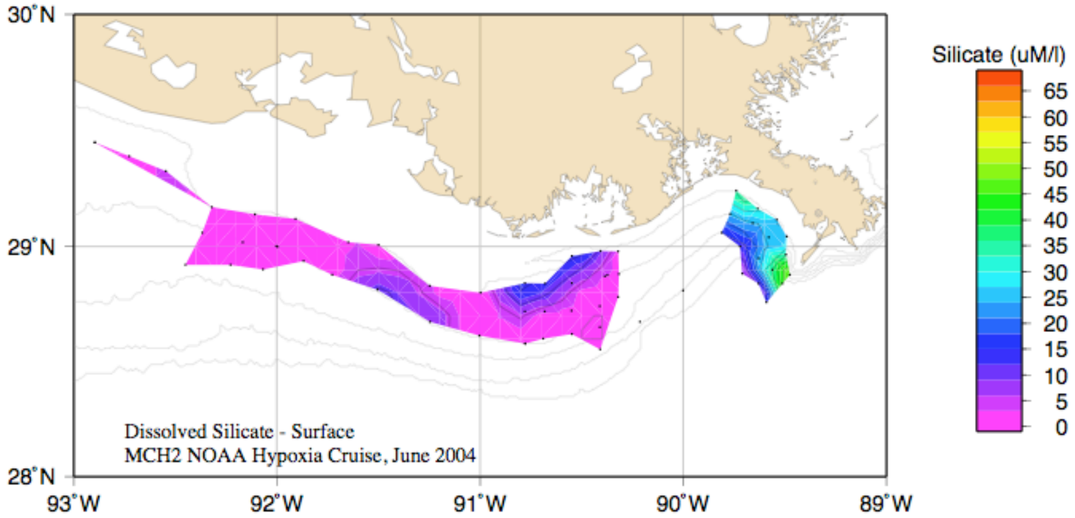

Figure A20. Surface plan view map of silicate – June

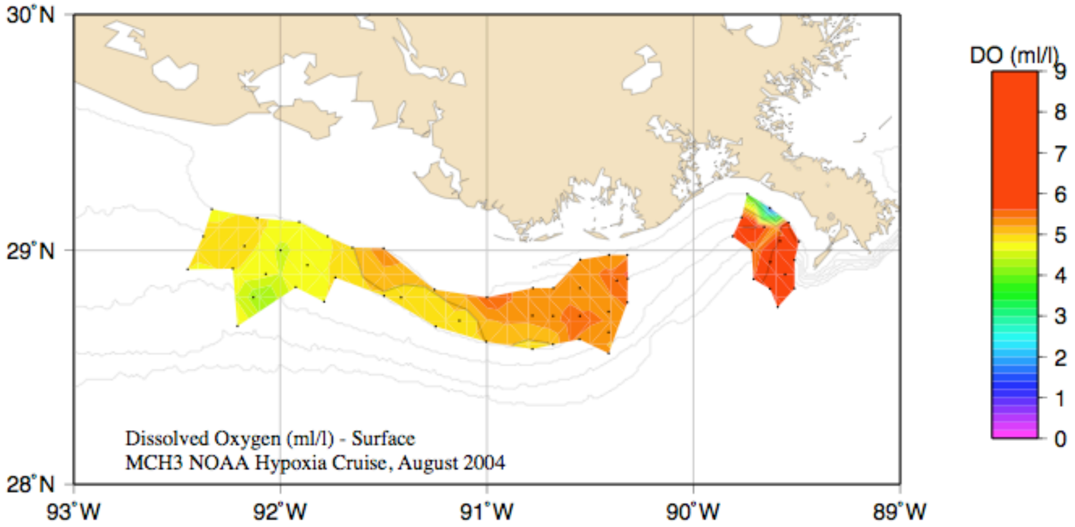

Figure A21. Surface plan view map of oxygen – August

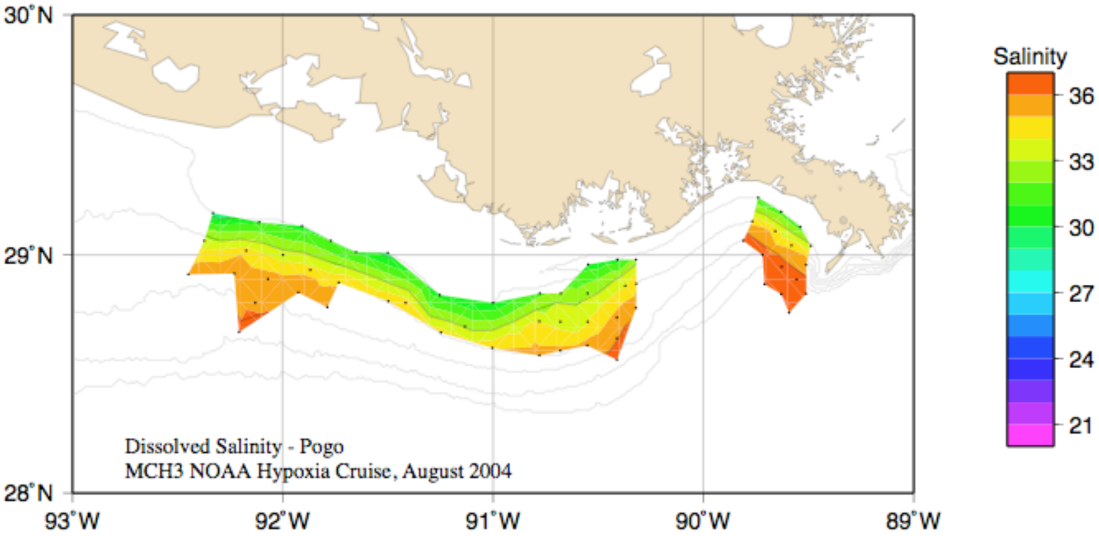

Figure A22. Bottom plan view map of salinity – August

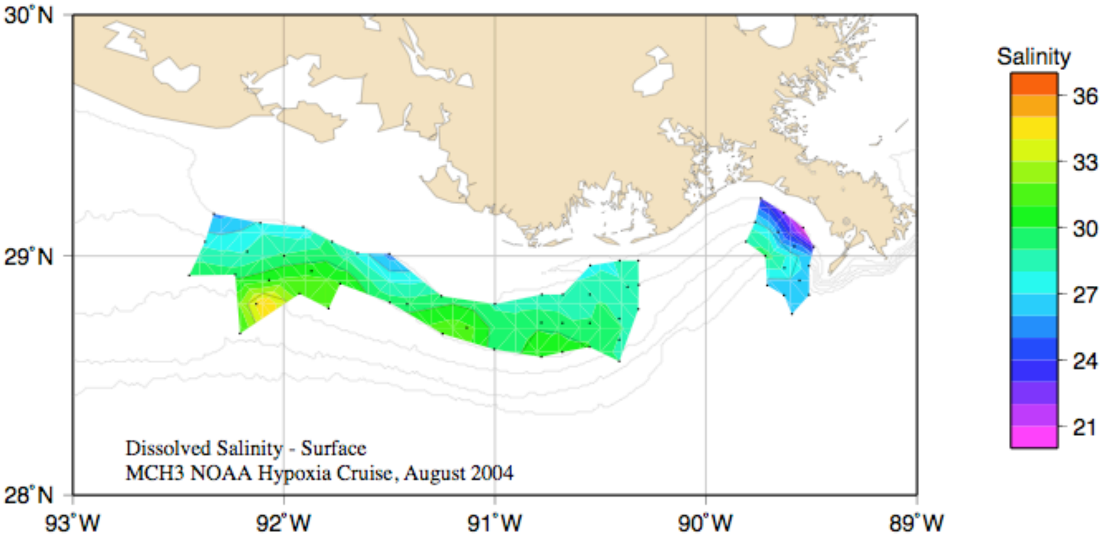

Figure A23. Surface plan view map of salinity – August

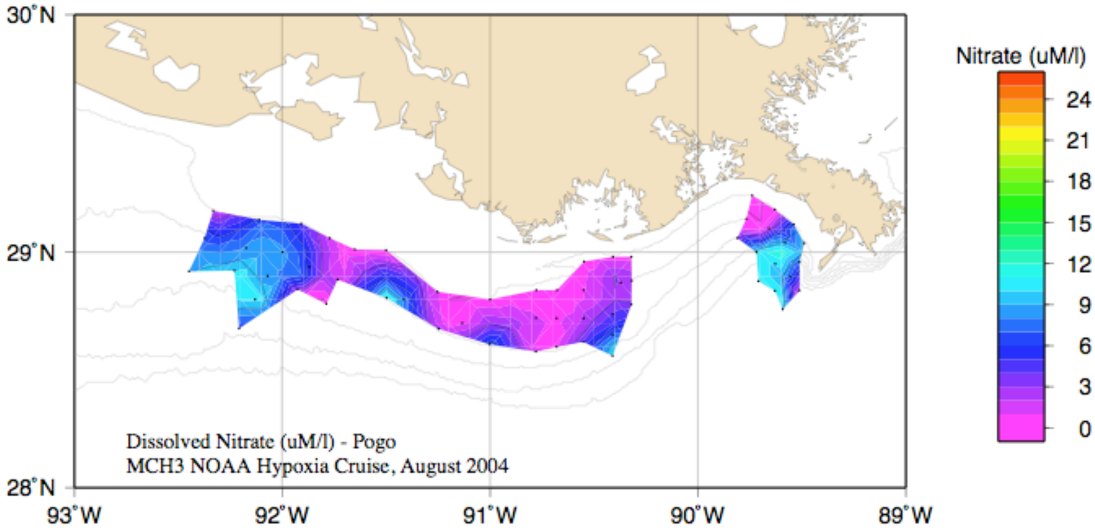

Figure A24. Bottom plan view map of nitrate – August

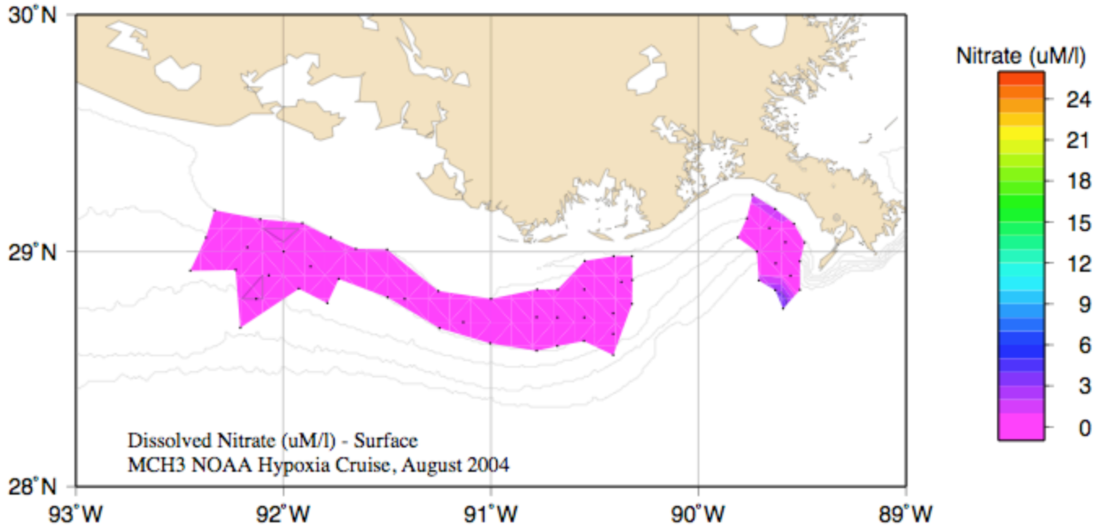

Figure A25. Surface plan view map of nitrate – August

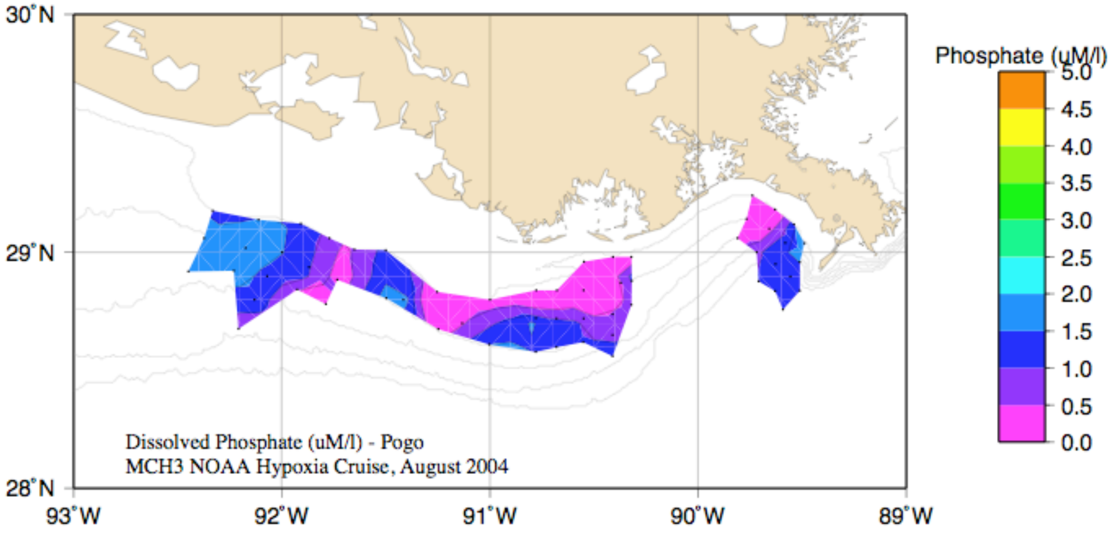

Figure A26. Bottom plan view map of phosphate – August

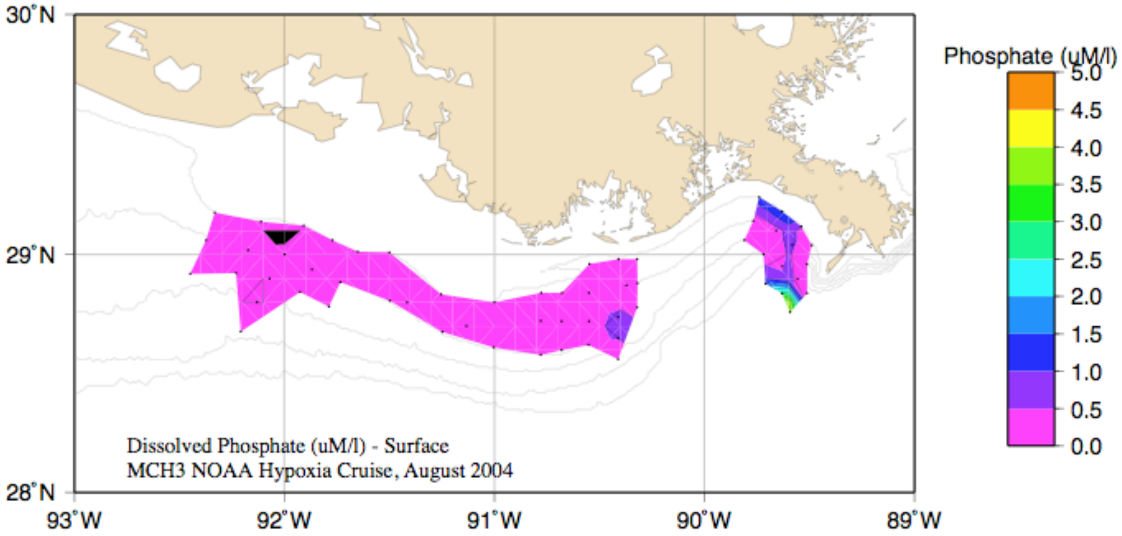

Figure A27. Surface plan view map of phosphate – August

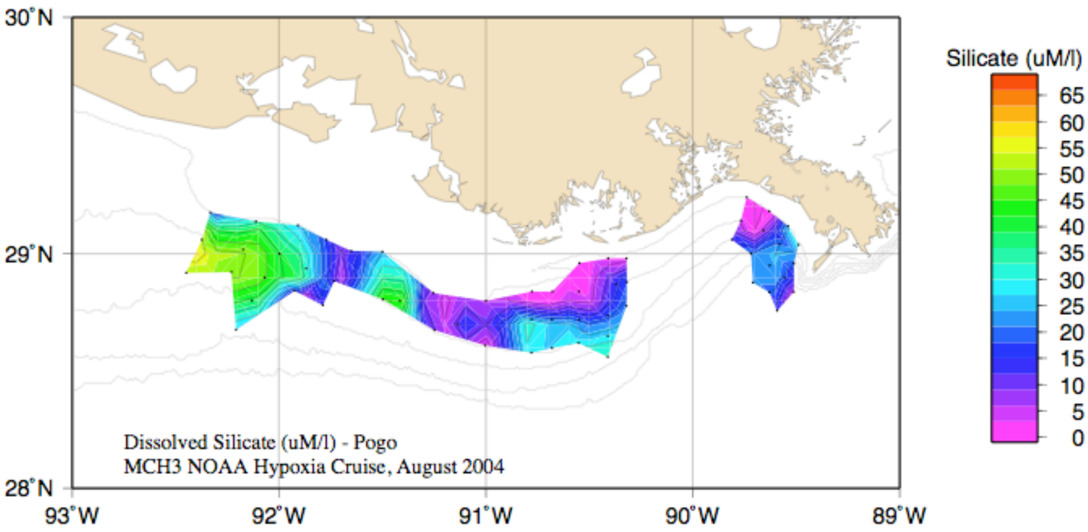

Figure A28. Bottom plan view map of silicate – August

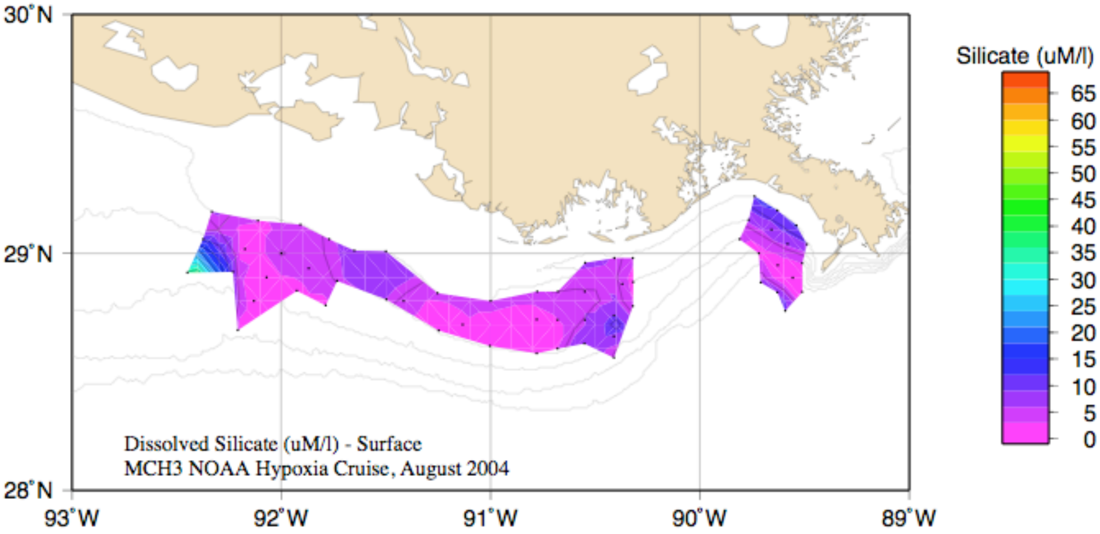

Figure A29. Surface plan view map of silicate – August

VITA

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