RELATIONSHIPS OF LIGHT TRANSMISSION, STRATIFICATION, AND FLUORESCENCE IN THE HYPOXIC REGION OF TEXAS-LOUISIANA SHELF IN SPRING/SUMMER 2009

A Senior Scholars Thesis

by

JENNY LOUISE TOWNS

Submitted to the Office of Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

April 2010

Major: Environmental Geoscience

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ABSTRACT

Relationships of Light Transmission, Stratification, and Fluorescence in the Hypoxic Region of Texas-Louisiana Shelf in Spring/Summer 2009. (April 2010)

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The growth of phytoplankton in hypoxic waters requires nutrients and light. In river plumes of the coastal ocean, river borne surface nutrient concentrations decrease with distance from the river mouth. Light availability at the surface also changes with distance from the river source, as particulates and other materials sink through the water column. Using in situ CTD sensors, water samples of nutrients, and ship flow-through data from two Louisiana Shelf research cruises, April and July 2009, the relationship between transmissivity, photosynthetically available radiation (PAR), stratification, and fluorescence are analyzed. PAR is measured using a silicon photovoltaic detector and is measured in the 400 to 700 nm range. A fluorometer is used to measure the fluorescence of chlorophyll *a* in µg/L and is a proxy indicator for phytoplankton biomass. The Louisiana Shelf is home to the largest hypoxic zone in the western hemisphere, covering on average more than 15000 sq. km. The Louisiana hypoxic zone occurs seasonally in summer and is typically dissipated by physical processes in fall. Hypoxia is defined as waters that have a dissolved oxygen concentration of 1.4 ml/L and is the level at which marine organisms are typically adversely affected. Preliminary results show expected relationships between transmissivity and fluorescence in the water column indicating a positive correlation between light availability and fluorescence. The spatial distribution of stratification, light availability, fluorescence, and nutrients are compared for the different seasons.

ACKNOWLEDGMENTS

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I would also like to thank the graduate students working under Dr. DiMarco who have given me assistance in MATLAB programming: Stuart Pearce and Ruth Mullins. I would also like to thank Manish Jain from the Electrical Engineering Department for the assistance he has provided in creating codes to generate the CTD profiles.

Last but not least, I would like to thank my parents and my boyfriend for their continuous support and encouragement.

NOMENCLATURE

CTD	Conductivity, Temperature, Depth
CSCOR	Center for Sponsored Ocean Coastal Research
GHAP	Gulf Hypoxia Action Plan
MCH	Mechanisms Controlling Hypoxia
NGOMEX	Northern Gulf of Mexico
NOAA	National Oceanographic and Atmospheric Association
PAR	Photosynthetically Available Radiation

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CHAPTER I

INTRODUCTION

Of the three main anthropogenic problems facing the oceans today (overfishing, acidification, and eutrophication), eutrophication is the most regionally concentrated, yet globally reaching. Eutrophication occurs when excessive nutrients accumulate in a body of water and spur algae growth, which, in turn, depletes the oxygen as the plant material decomposes. This process occurs in areas called hypoxic zones, where measured dissolved oxygen concentrations are 1.4 mL/L or less [*Bianchi et al*., 2010]. Under these conditions it is difficult to sustain marine animal life. Hypoxic zones (popularly called "dead zones") occur all over the world and now number in the hundreds, affecting an area of around 245,000 square kilometers of ocean [*Diaz and Rosenberg,* 2008]. Within these zones delicate estuaries and marine ecosystems struggle for survival and the demersal fishing industries decline. The Chesapeake Bay, located near the states of Maryland, Delaware and Virginia, is the largest estuary in the United States and has been an observed hypoxic area since the 1930's. The detriment to this region in terms of a decline in benthic macrofauna and disappearing tidal marshes is evident in the mortality of fisheries and diseases associated with them [*Kemp et al.*, 2005].

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

The northern Gulf of Mexico hypoxic zone is localized around the mouths of the Atchafalaya and Mississippi rivers and has covered more than 15,000 square kilometers annually since 1993 [*Rabalais et al.*, 2002]. One of the problems normally associated with hypoxic zones is a decline in fish catches; however, this has not been the case for the northern Gulf of Mexico hypoxic zone. This reason for this is that the main species that are being fished spend the critical juvenile stages of their life cycles in estuarine environments each year prior to the development of the hypoxic conditions. In general, the commercially important species are not spatially or temporally connected to the hypoxic zones during the critical stages of their life cycles [*Bianchi*, 2008].

One of the main physical factors contributing to the formation of the Gulf of Mexico hypoxic zone in the summer is the stratification of the water column that occurs near the mouth of the Mississippi and Atchafalaya rivers. Two distinct layers form when the fresh water input from the rivers drains into the gulf creating a less dense layer of water, which rests on top of the denser saltwater layer [*Hetland and DiMarco*, 2008]. These layers become very stable in the summer and are not prone to mixing without some other physical forcing, such as wind, upwellings, or hurricanes. Therefore, an influx of nutrients to the surface layer stimulates an increase in primary algal production that causes an increase in organic matter that goes to the denser layer below the pycnocline. This causes an increase in respiration in the lower, denser layer, which results in decreased dissolved oxygen concentration. The types of nutrients that spur algae growth are nitrates and phosphates derived from fertilizer from agricultural operations [*Bianchi*, 2010]. This, and other types of Mississippi runoff constitutes an estimated mean annual flux of 1.2 million metric tons of nitrogen and 0.15 million metric tons of phosphorus [*Bianchi*, 2010]. There is speculation that other sources of organic matter, namely labile and refractory materials derived from coastal and deltaic sediments contribute to the formation of the hypoxic zone [*Bianchi*, 2008]. The rates of denudation of coastal ecosystems and wetlands near the Mississippi are some of the highest in the United States. The result is an increase in the nonriverine organic matter flux that contributes to oxygen depletion [*Bianchi,* 2008]. In addition, the alterations to the natural wetlands by the Army Corp. of Engineers are partly responsible for the loss of wetlands in this area and thus increased erosion.

In response to the perplexing issue of hypoxia in the northern Gulf of Mexico, a Gulf Hypoxia Action Plan (GHAP) has been developed to mitigate, control and reduce the size of the hypoxic zone. The main goal established by the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force was to reduce the size of the hypoxic area to 5,000 sq. km by 2015 [*Mississippi River/Gulf of Mexico Watershed Nutrient Task Force*, 2008]. The U. S. Environmental Protection Agency's Science Advisory Board (SAB) has recently reviewed the plan for reduction of hypoxia but has retained the same goal of reduction in size as the Task Force. This number was chosen arbitrarily by researchers and does not reflect any findings or data that would suggest whether or not this is a beneficial result to be desired in terms of the effects this would have on the ecosystem [*Bianchi*, 2008]. Further research is currently being conducted on what may be more appropriate or suitable goals for reduction of the hypoxic area. Part of this research includes investigating the physical factors that influence the size, shape and distribution of hypoxia along the Texas and Louisiana coast.

There is still much to understand about the complex interactions of nutrient input, physical factors and the unique topography and hydrography of the Louisiana coast. Not surprisingly, the predicted size of the hypoxic area for last summer was expected to be one of the biggest on record; however, it was the fourth smallest on record.
This erroneous prediction reflects the ongoing lack of understanding of the processes that control hypoxia. Although it has been studied for over thirty years, scientists still have a limited understanding of the factors that control this system. My research will focus on only a small part of the total research that's being done on this largely perplexing problem.

Fundamentally, there are two components necessary for the growth of phytoplankton: nutrients and light. Light is the other important factor to be considered for the Mississippi plume area, where discharge from the river is the highest. According to *Cloern's* [1999] paper on the importance of light for phytoplankton growth, the photic zone of the plume is shallow and since nutrient concentrations remain at a high level there, changes in primary productivity can be correlated to light availability. Light transmission is measured as photosynthetically available radiation or PAR in $\mu mol/m^2/s$. This is a measure of irradiance of light as it penetrates down the water column and is scattered and absorbed causing a reduction in irradiance. The vertical attenuation of the light is accounted for with an extinction coefficient that is part of the formula to calculate irradiance $E_d(z) = E_d(0)e^{-Kdz}$, where K_d is the vertical attenuation coefficient for downward radiation [*Kirk*, 1994]. It is expected that the further the distance from the hypoxic area the more light penetrates the water column due to a reduction in organic matter, which attenuates the light. Fluorescence is a proxy for chlorophyll *a* in the water, which in turn is a measure of the biomass.

In my research I aim to characterize the spatial and temporal variability of hypoxia based on the difference in two seasons (spring and summer) and the hydrographic and topographic variability based on the areas sampled in spring and summer of 2009.

CHAPTER II

METHODS

The observational data presented here from the MCH 13 and MCH 14 cruises (dates April 4th-8th 2009 and July 27th – 30th 2009 respectively) was collected in situ aboard the R/V Pelican using a Seabird SBE 9 CTD/rosette system. See Table 1.1 below for summary of data collected.

Table 1.1 Summary of Cruise Data and Recorded Properties

Cruise	Date	No. of Stations	Properties	Units
MCH 13	April 4th -8th 2009	32	Salinity	PSS-78
			Temperature	° C
			Dissolved Oxygen	mL/L
MCH 14	July 27th – 30th 2009	30	Transmissivity	Percent (%)
			Fluorescence	µg/L
			PAR	µmol/m^2/s or microeinsteins/m^2/s

Data collection

The CTD/rosette system was equipped with eighteen, five-liter and fifteen, twenty-liter niskin bottles, General Oceanics Model 1010, which were used to collect samples from the water column. Each niskin bottle is connected to a wire, which can be tripped remotely, closing the bottle after collection of water, as the rosette moves upward through the water column. Samples were collected near the surface at about 1.5 meter depth, near the bottom, at about 0.5 m above the bottom and at 5 m depth intervals. Salinity samples were collected in 200 mL glass bottles that were preconditioned by triple rinsing them with sample water before collection. Salinity samples were analyzed aboard the ship using a Guildline Model 8400 Autosal Laboratory Salinometer. This system measures a conductivity ratio relative to seawater. Each sample is measured three times to ensure accurate analysis. The salinity sample is held at a constant temperature in a water bath while the conductivity ratio is measured. The conductivity and temperature are then used to calculate the salinity on the practical salinity scale using the equation for practical salinity given in *Fofonoff and Millard* [1983].

Samples were also analyzed for dissolved oxygen using the microWinkler technique [*Carpenter*, 1965]. The procedure requires sampling seawater from the niskin bottle into a glass flask without allowing any atmospheric oxygen to be trapped in the bottle. The sample is titrated with a mixture of manganese hydroxide ($Mn(OH)_3$) and alkaline iodide (I^-) to fix the oxygen in the sample. After the oxygen is trapped the sample is acidified and then titrated using sodium thiosulfate solution to find the concentration of I_3^- ions formed. This method has a precision of 0.01 mL/L oxygen at STP.

Photosynthetically Available Radiation (PAR) or irradiance was measured using a silicon photovoltaic detector in the 400 to 700 nm range, which is the range of light waves required for photosynthesis by primary producers. The instrument used was a Biospherical Instruments 2-QSP-200L model. Fluorescence was measured using a Chelsea Instruments Aquatraka II model fluorometer. The fluorescence of chlorophyll α in phytoplankton was measured as blue green light. Transmissivity is the measurement of the percentage of light that can penetrate through the water column and is the inverse of light absorbance. The instrument used to measure transmissivity is called a transmissometer from Wetlabs with a 10 cm path length. Light is shone from a light in one end of the cylinder to the opposite end where a receiving component registers the light transmission as conductivity, which is measured in volts. All apparatus described above are attached to the CTD rosette and deployed over the side of the ship.

Continuous measurements of salinity and temperature were made using a thermosalinograph with water intake located in the ship's bow at about 3 m depth. Continuous dissolved oxygen concentrations were measured using a Seabird SBE 43 oxygen probe [*DiMarco*, 2009]. The continuous dissolved oxygen probe measurements were compared against the values obtained from the widely accepted and accurate microWinkler titration technique. The oxygen probe was calibrated according to the dissolved oxygen values from the titration. Also, as part of the data processing a relationship may be established between the oxygen probe values and the microWinkler titration values and a constant can usually be multiplied by the oxygen probe values to correct them if necessary.

Data processing

The data was collected aboard the ship and input into the computer. Once back on land, the raw data was processed. The SBE Data Processing software converts raw data from the SeaSave program into readable cnv files. The upcast data, or the data obtained from the rosette's ascension through the water column was discarded for the purposes of my research. This is because upcast data contains less accurate probe readings due to the turbulence created around the sensitive dissolved oxygen measuring instruments. A range of +2 seconds to +5 seconds for the SBE 43 dissolved oxygen center was entered. Values from one meter depth intervals were selected from the raw data files and all else was discarded.

CHAPTER III

RESULTS

Conductivity, temperature and depth profiles for the MCH 13 and MCH 14 cruises, April and July 2009 respectively, were created to illustrate the relationship between dissolved oxygen, temperature, salinity, sea temperature, PAR, and light transmission. Comparisons were made between vertical profiles of stations at the same location for the different seasons. The meteorological conditions during the spring are such that frequent storms cause a decrease in vertical stability, causing an increase in mixing of the surface freshwater layer and the lower saltwater layer. During the summer, vertical stability increases and stratification of the freshwater layer and lower, saltwater layer dominates. Sampling is done at predetermined stations based on the isobath contours. The maps in Figures 3-1 and 3-2 show the location of the stations where sampling occurred. The study area can be divided into three main sections based on the coastal topography. The most eastern part of the maps shown in the figures below is near the Mississippi River delta. This is where the highest flux of freshwater comes from and presumably the largest amount of stratification occurs here due to that. The middle section of the map and corresponding station locations is near Terrebonne Bay. The last area of interest on the map is located in the most western part of the sampling area and is in close proximity to the Atchafalaya River basin. It is a distributary of the Red River and the Mississippi River. Thus, the plume that develops from the flux of water from the Atchafalaya into the Gulf of Mexico is similar in chemical composition to the Mississippi River plume.

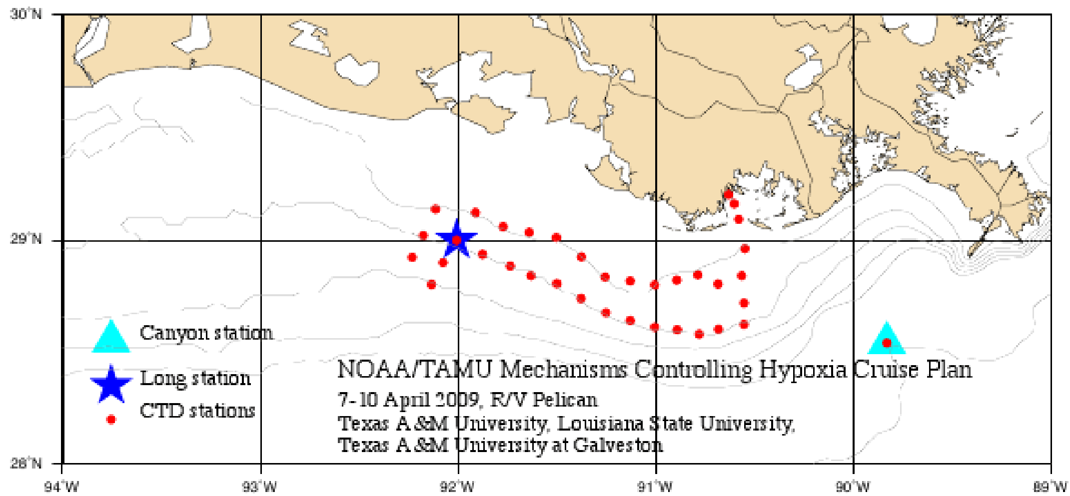

Figure 3-1. Map of Mechanisms Controlling Hypoxia cruise no. 13 in April 2009. Isobaths shown are 10, 20, 30, 40 and 50m.

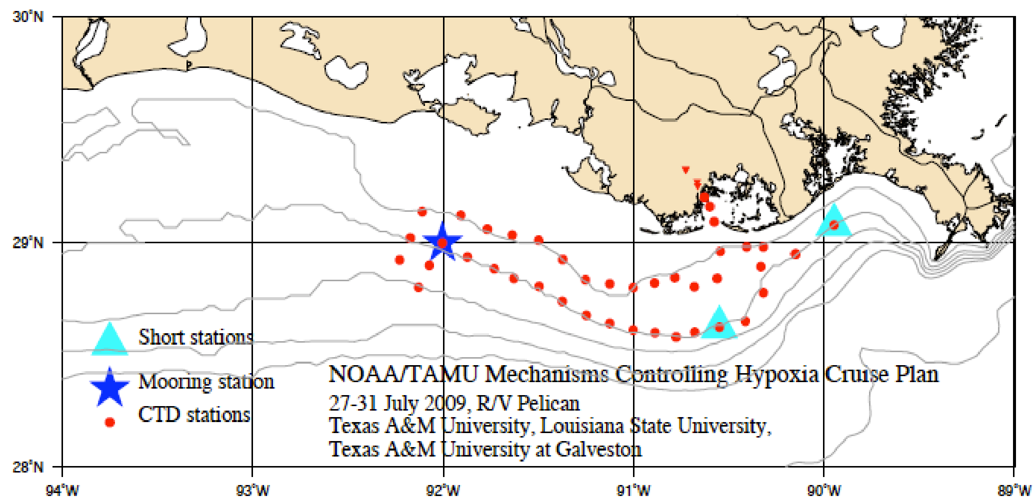

Figure 3-2. Map of Mechanisms Controlling Hypoxia cruise no. 14 in July 2009. Isobaths shown are 10, 20, 30, 40 and 50m.

Latitude and longitude is recorded at each station to mark the exact location of sampling for each station. To gain a better understanding of seasonal variability station 4b vertical profiles for the April cruise and July cruise were compared. See Figures 3-3 and 3-4 below. In Figure 3-4 the hypoxia is denoted by the shaded red area where dissolved oxygen falls below 1.4 mL/L. In both figures PAR, fluorescence, and dissolved oxygen parameters follow the same trends in the water column. Sea temperature, which is represented by the black line in both figures, has an apparent reversal in trends between the month of April and the month of July. This is due to the high heat capacity of seawater (3985 J/kg K), allowing the water to stay warmer at depth while the surface cools due to seasonal atmospheric conditions. In the summer the thermocline reverses in direction as warm water at the top gradually becomes cooler with depth.

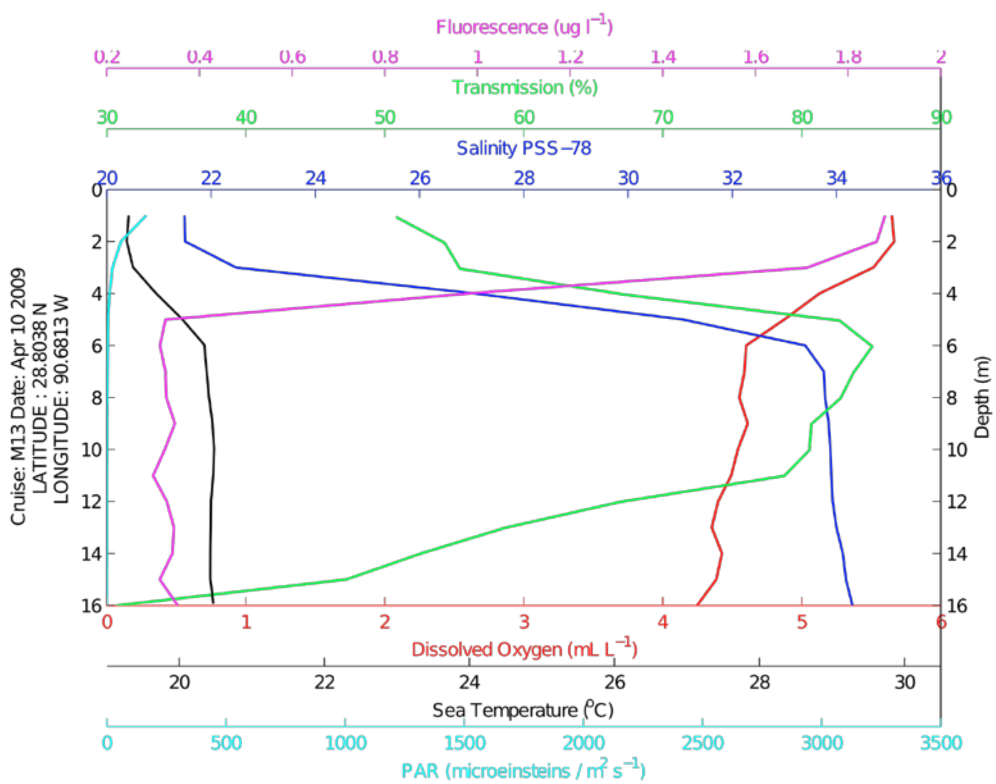

Figure 3-3. CTD profile for station 4b for MCH 13 cruise in April of 2009.

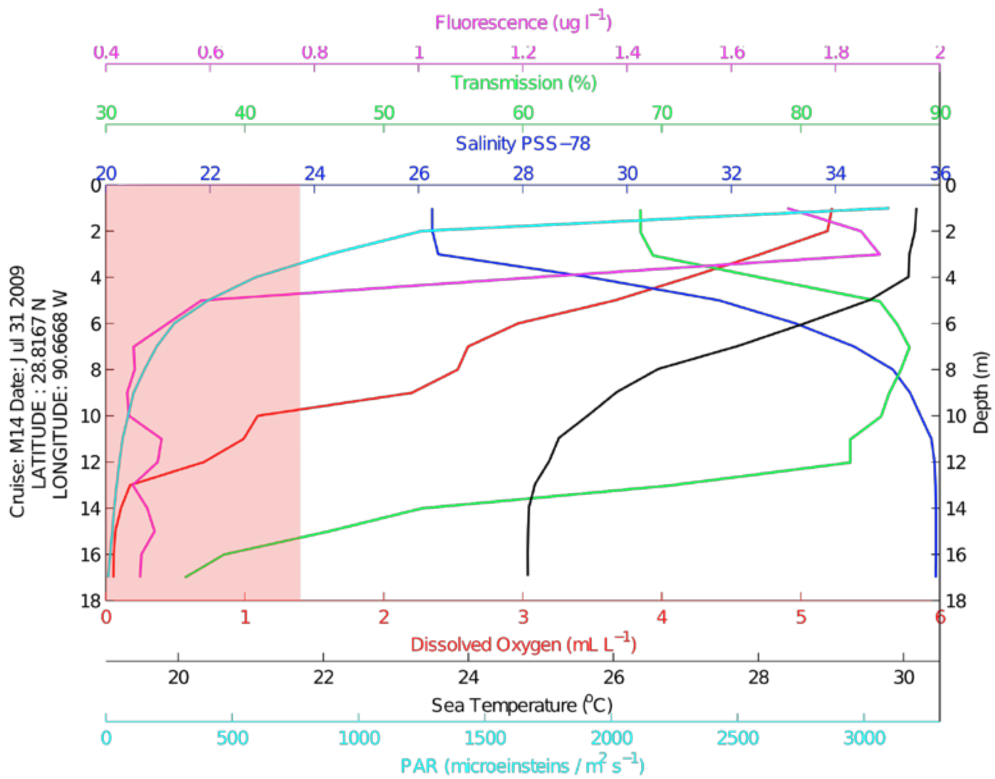

Figure 3-4. CTD profile for station 4b for MCH 14 cruise in July of 2009. Note the red shaded area that indicates the values of dissolved oxygen below which hypoxia occurs.

The percentage of transmission of light appears to increase in the surface layer (0 – 5 m depth) and sharply decrease from about 14 m to the bottom. This is expected as the amount of organic matter below the pycnocline increases in both the spring and summer causing a physical clouding of the water.

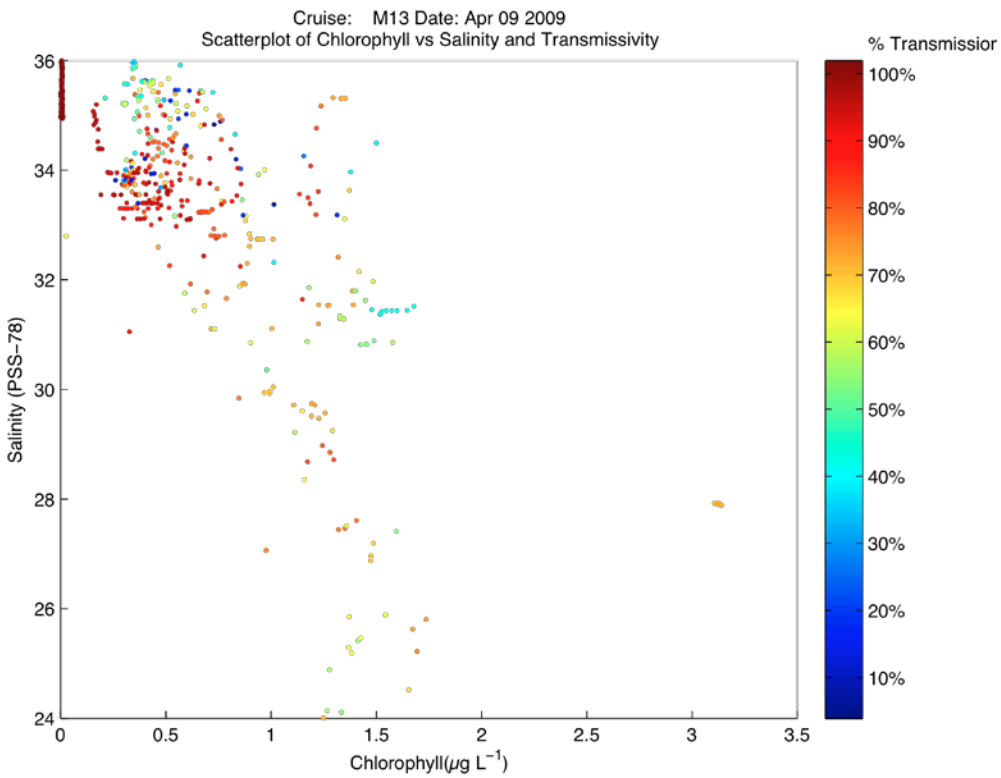

Figure 3-5. Scatterplot of chlorophyll vs salinity and transmission for MCH 13 cruise.

Figures 3-4 to 3-8 demonstrate the difference in distributions of salinity, chlorophyll, transmission and their relationship to one another. Figures 3-4 and 3-5 indicate that for lower chlorophyll values transmission is the highest, ~90%. This is related to the decrease in primary productivity of algae that grow primarily in the nutrient rich

freshwater layer above the pycnocline. Thus, the least amount of particles and organisms in the water column at this point allow light to penetrate the most.
It is clear from Figures 3-7 and 3-8 that high salinity values occur in the summer as opposed to the spring. Also, high salinity values correspond with low chlorophyll values. There appears to be two trends of data in Figure 3-8, which represents the summer cruise data, where high salinity, low chlorophyll and medium to high transmission likely represent data sampled from stations not in close proximity with either the Atchafalaya or the Mississippi Rivers. The second trend in the data appears to be defined by low salinity, high chlorophyll and high transmission. This is likely associated with the Atchafalaya and or Mississippi freshwater plumes.

In addition to plotting the data for the variables of interest for both cruises to understand the relationships between them, another analytical method can be employed to observe the seasonal variability of the two data sets. It begins with calculating the Brunt Väisälä frequency, represented by N^2 in this equation: $N^2 = -g/\rho\ (d\rho/dz)$, where g is acceleration due to gravity, ρ is density of the water column and z is depth. N^2 is in units of s^{-2}. The Brunt Väisälä frequency is a measure of vertical stratification in the water column. It is the vertical frequency excited by a vertical displacement of a parcel of fluid [*Stuart*, 2008]. Comparing the maximum Brunt Väisälä frequency that occurs at each station to the apparent oxygen utilization at each station (100% saturation concentration minus observed bottom dissolved oxygen concentration) the seasonal variability is apparent. Appparent oxygen utilization (AOU) accounts for the effects of temperature on the amount of saturation possible for dissolved oxygen in the water column. Therefore, it is a better way of quantifying the amount of dissolved oxygen utilized by organisms in the water. In Figure 3-9 there is a dichotomy between the two seasons (spring and summer). The lowest AOU values occur for the spring data set and correspond to a range of N^2 values from 0 to 0.09 s^{-2}. The summer values show higher AOU values as expected and a range of N^2 values from 0 to 0.04. Higher N^2 values occur when there is a higher frequency in the oscillation of the fluid parcel in the water column. This is associated with a higher vertical stratification or stability of the water column. The high N^2 values that occur for the spring data set are due to the stability of the water column above the pycnocline, where a high influx of freshwater from the Mississippi and Atchafalaya is occurring. Typically, a high maximum N^2 value occurring at the depth of the pycnocline (~10m) in the summer indicates greater stability.

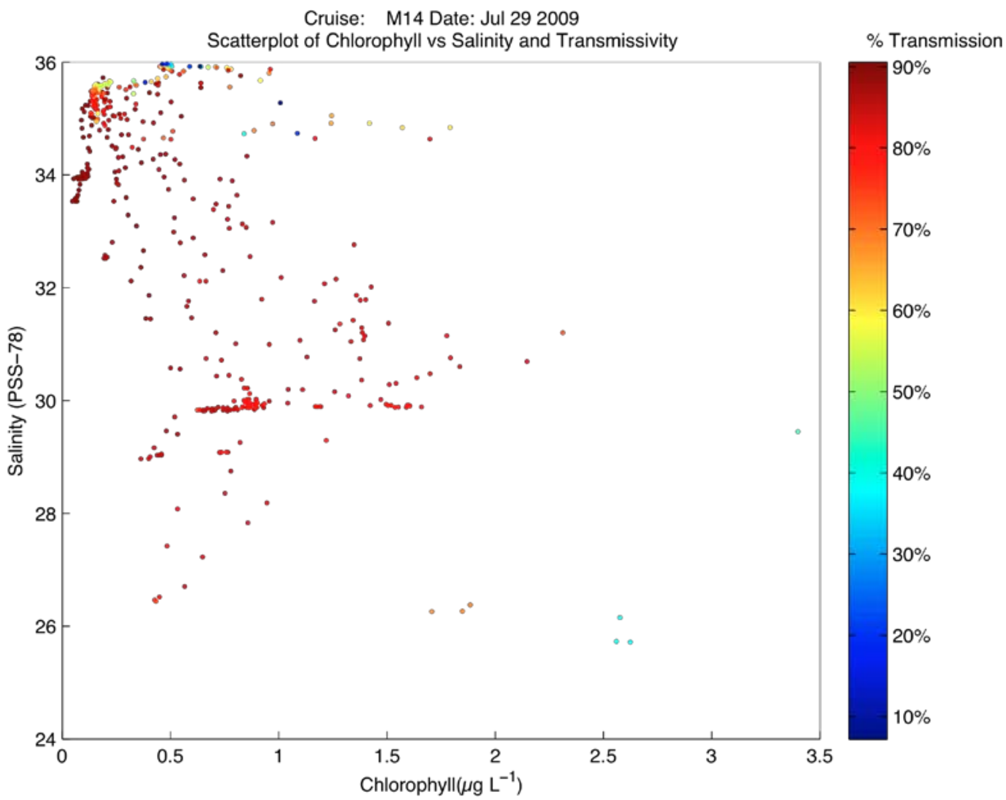

Figure 3-6. Scatterplot of chlorophyll vs salinity and transmission for MCH 14 cruise.

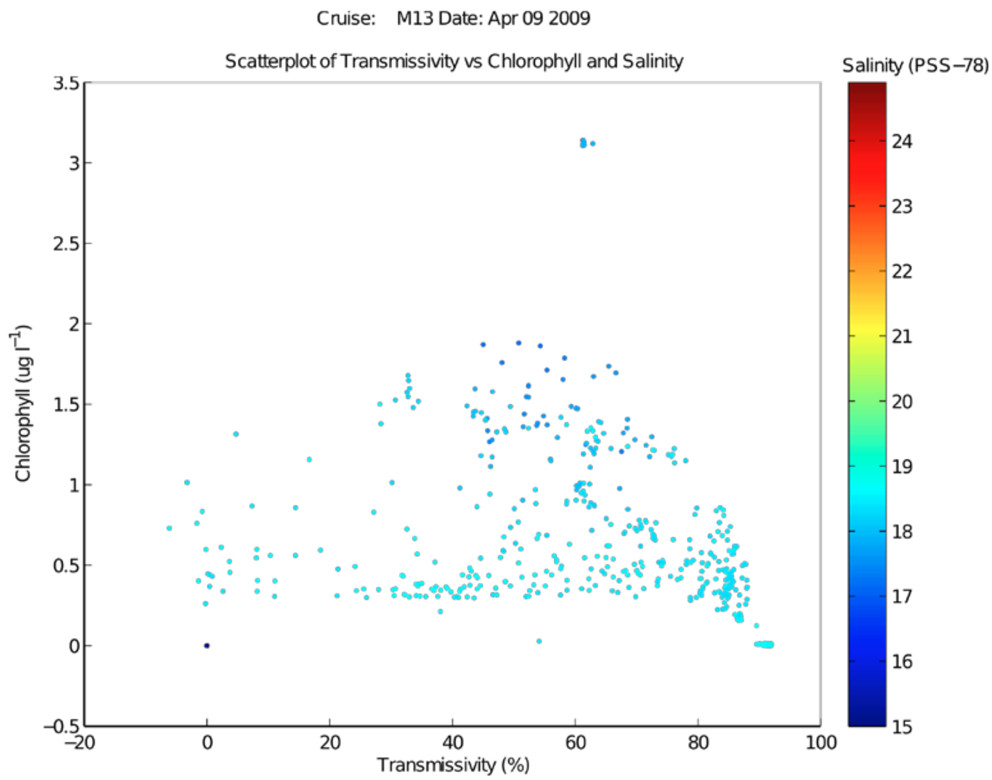

Figure 3-7. Scatterplot of transmission or transmissivity vs chlorophyll and salinity for MCH 13 cruise.

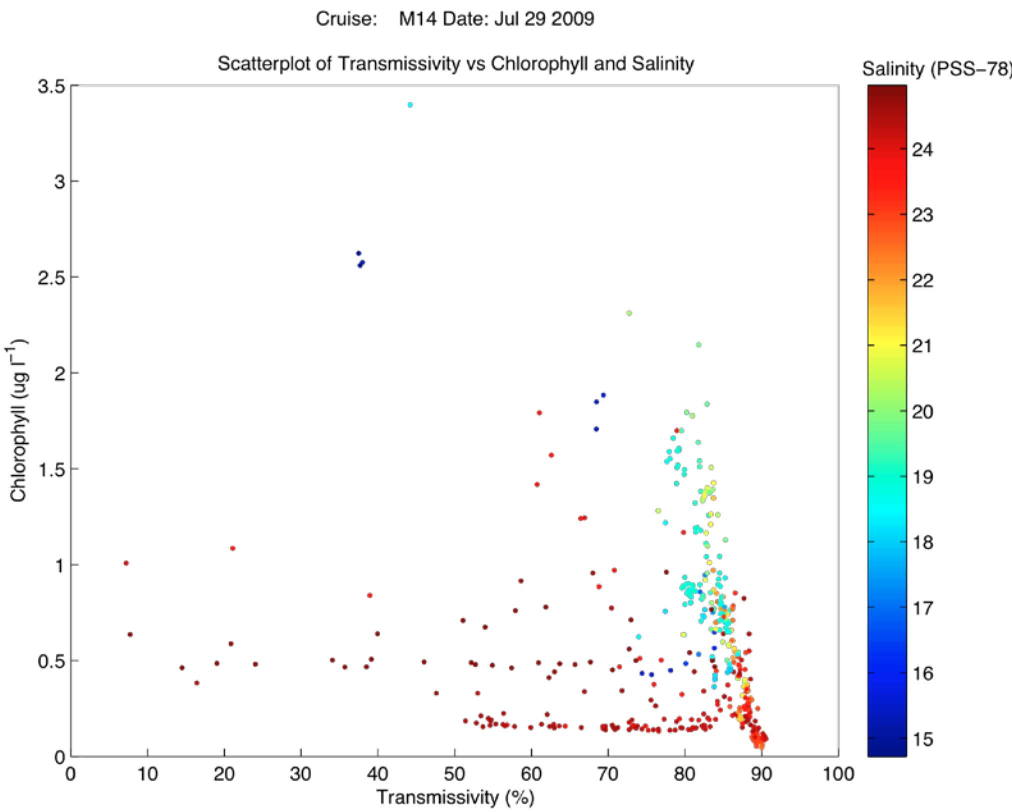

Figure 3-8. Scatterplot of transmission or transmissivity vs chlorophyll and salinity for MCH 14 cruise.

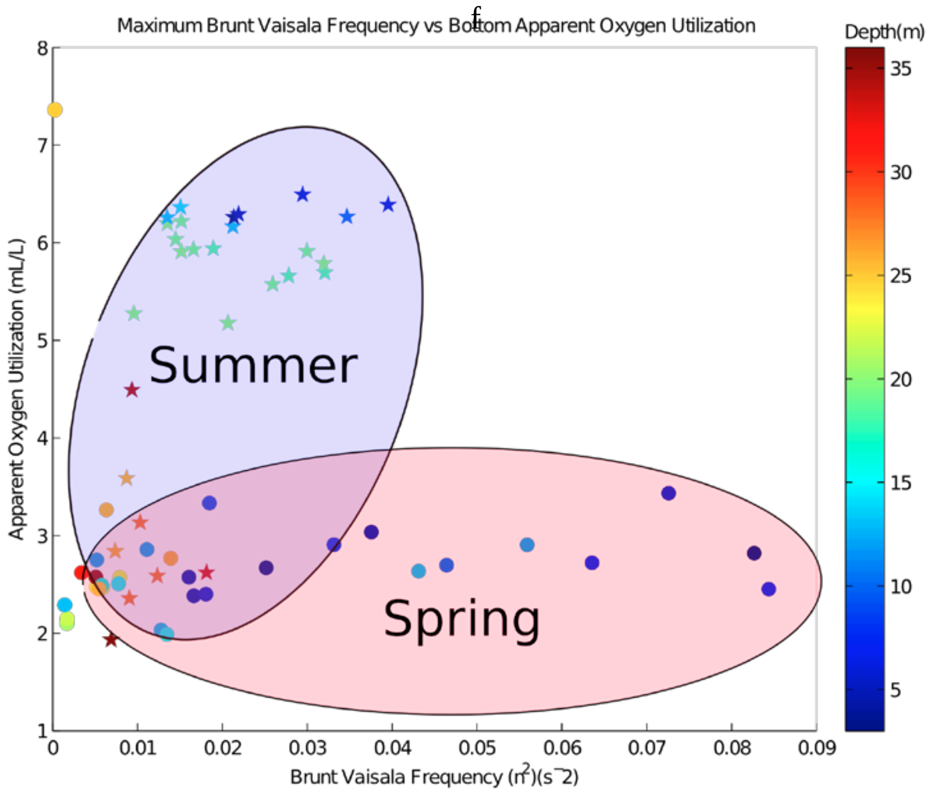

Figure 3-9. Scatterplot of maximum Brunt Väisälä frequency (n^2) vs the apparent oxygen concentration for MCH 13 and 14. The spring values (MCH 13) are indicated by the star symbols and the summer values (MCH 14) are indicated by the dots. The markers are colored according to the depth at which the maximum n^2 value occurred in the water column.

CHAPTER IV

CONCLUSIONS

The seasonal and spatial variability of the hypoxic area was examined in this study. The problem of hypoxia in the northern Gulf of Mexico is not strictly controlled by nutrient flux from the Mississippi. The physical factors, such as local wind forcing, hydrography and local topography are equally important in determining the size and extent of hypoxia. What is unknown about hypoxia controls greatly outweighs what is known. Further study into the ecological implications of this problem is also needed to make predictions and policy to better serve the ecosystem of the northern Gulf of Mexico and ultimately the well being of the people that reside near this part of the Gulf Coast. The parameters of hypoxia analyzed in this study are indicators of the severity as well as the extent of hypoxia. Trends must be observed from year to year to gain a better understanding of how the hypoxic area changes throughout the seasons and over the course of time, as meteorological and oceanographic cyclic variations may have unseen effects on the development and dissipation of hypoxic conditions. Each hypoxic area is unique to its local environment and may not have similar characteristics or controls as any other hypoxic area in the world. This is why it is important to continue studying the hypoxic area of the northern Gulf of Mexico in hopes of being able to characterize the processes that control it more accurately in the future.

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