THE ROLE OF PARTICULATE MATTER IN THE DEVELOPMENT OF HYPOXIA ON THE TEXAS-LOUISIANA SHELF

A Thesis

by

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ABSTRACT

In the northern Gulf of Mexico, hypoxia occurs annually during the summer on the Texas-Louisiana shelf. This study examines the distribution of particulate and dissolved components relative to hydrography, to better understand the processes controlling the development of hypoxia.

Particulate matter on the Texas-Louisiana Shelf has three major sources – river plumes, primary production, and resuspended sediments. The sources and processes controlling distribution and transport of particles are investigated using optical proxies (backscattering, chlorophyll fluorescence, Colored Dissolved Organic Matter fluorescence (CDOM)), temperature, salinity, dissolved oxygen (DO), and in-situ sampling during June and August 2011 cruises of the Mechanisms Controlling Hypoxia program (hypoxia.tamu.edu). Discrete samples of particulate matter (PM) and particulate organic carbon (POC) concentration were obtained for analysis and calibration of optical instruments interfaced with a profiling CTD, a towed undulating CTD (Acrobat), and the ship’s flow-through system along the shelf from south of Galveston, Texas, to east of the Mississippi delta.

The results of this study support a previously hypothesized concept of three primary areas of organic and inorganic particle composition and processes that dominate those areas – river-dominated water, highly productive surface waters, and clear, nutrient-poor low-productivity surface waters. The distribution and bulk composition of particulate matter in the northern Gulf of Mexico, plus the distribution
of chlorophyll fluorescence and CDOM suggest that subpycnocline primary production plays a role in determining oxygen concentration in subpycnocline waters away from the river-dominated water.
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Finally, thanks to my parents for their love and encouragement.
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INTRODUCTION

Background

Hypoxic zones affect as many as 400 regions throughout the world, totaling an area of about 245,000 square kilometers of the Earth’s oceans (Diaz and Rosenberg, 2008). They form after seawater in the euphotic zone becomes loaded with nutrients, creating an increase in algal growth. The organic material settles and decomposes, utilizing oxygen in the water column or at the seafloor. When the dissolved oxygen concentration decreases to less than 2 mg l$^{-1}$ (1.4 ml l$^{-1}$), conditions become stressful to heterotrophic organisms and the area is referred to as hypoxic (Rabalais et al., 2010; Bianchi et al., 2010). This condition can sometimes be found at mid-water depths beneath areas of high surface productivity along continental margins, but more frequently occurs near the seafloor where there is an abundance of organic matter (Rabalais et al., 2001).

In the northern Gulf of Mexico (NGM), hypoxia is an annually recurring problem on the Texas-Louisiana shelf (Rabalais et al., 1996; Nowlin et al., 1998; Dale et al., 2010; Bianchi et al., 2010). It has been directly documented in this region since 1972 (Rabalais et al., 2001), and by proxies in sediment cores for over 1000 years, with a marked modern increase since the 1950’s (Sen Gupta, 1996; Osterman et al., 2005; Swarzenski et al., 2008). Over time, the area of hypoxia has grown significantly, with large inter-annular variability, depending partly on the total discharge of water from the Mississippi and Atchafalaya River system. Typically the hypoxic area is larger in flood
years and smaller in drought years and hurricane/storm years (Turner et al., 2006; Turner et al., 2008; http://toxics.usgs.gov/hypoxia/mississippi/oct_jun/).

The area of hypoxia in the NGM can cover over 15,000 square kilometers (Rabalais et al., 2002), mainly near the outflows of the Mississippi and Atchafalaya Rivers, which drain 41% of the contiguous United States (Milliman and Meade, 1983). Hypoxic waters are most prominent near the seafloor where water depths are 5 to 30 meters, but can be found as deep as 60 meters (Rabalais et al., 2001) (fig. 1). The bathymetry of the continental shelf allows the hypoxic area to extend further offshore in the shallow central and western regions of the Louisiana shelf than in the eastern region, where the Louisiana shelf is steeper and quickly transitions to the slope, thus minimizing the area of seafloor at depths where hypoxia typically occurs (Lahiry, 2007).

Unlike many hypoxic areas of the world, depletion of oxygen on the Texas-Louisiana shelf has had little to no documented affect on demersal fisheries (Bianchi, 2008). This may be because hypoxic areas form during the summer, and the species being commercially fished are not present in hypoxic regions during the early developmental phases of their lives (Bianchi, 2008). The economic and cultural impact of the shrimp and shellfish industry in this area of the Gulf of Mexico is extremely large, warranting a careful and continuing assessment of hypoxic conditions and causes.

The primary causes of hypoxia in this region have been shown to be a combination of spring nutrient loading (and subsequent carbon production, settling, and respiration near the seafloor) from the increased discharge of the Mississippi/Atchafalaya River system (Rabalais et al., 1996), physical stratification of
the water column from fresh water inflow and summer heating (Cochrane and Kelly, 1986; Hetland and DiMarco, 2008; Bianchi et al., 2010; Fennel et al., 2011), and east-west, north-south wind strength (downwelling vs upwelling) (Hetland and DiMarco, 2008; DiMarco et al., 2010; Forrest et al., 2011; Feng et al., 2012). Lehter et al., (2009) reported that the euphotic zone in the NGM often extends to the seafloor, allowing for primary production. Schaeffer et al., (2011) demonstrated that benthic production and respiration could serve as both a source and sink of oxygen in some regions and seasons, depending on light penetration below the pycnocline. They also found that the euphotic depth was correlated with the depth at which the water column turned hypoxic on the Louisiana shelf.

**Brown, Green, and Blue Waters**

Rowe and Chapman (2002) described three environmental zones on the Texas-Louisiana shelf that depended partially on the distance from the Mississippi River outflow but was based mostly on the “color” and ecological state of the water: Brown, Green and Blue (fig. 2). We will refer to these zones as “waters” to avoid the notion that these are fixed geographic boundaries. The Brown, turbid, sediment-laden water yields low rates of photosynthesis due to light limitation even in surface waters. In Green waters, most of the river-born inorganic and organic sediment has settled out (or has been filtered out by zooplankton), allowing for greater light penetration and increased photosynthesis in surface waters. Hypoxia in these areas is maintained by carbon loading from surface productivity and stratification. The area farthest from the river input -Blue
water - has extremely low particulate matter concentrations because not only have the river-born particles been removed, but primary production and marine biogenic particles are low because the nutrients have been utilized, leaving clear surface waters. When present, benthic hypoxia beneath Blue water is controlled by stratification according to the Rowe and Chapman (2002) scheme because ventilation of the subpycnoline is inhibited by water-column stability. In addition to the Mississippi River outflow, one must also consider the output of water from the Atchafalaya River and other wetlands along the Louisiana and Texas shelves (Bianchi et al., 2009). Distance from source waters refers to both along-shelf and across-shelf directions. Boundaries between the three water types are highly variable in both time and space and each area has different dynamics, leading to highly variable environments across the Texas-Louisiana shelf and throughout the water column.

As observed in Rowe and Chapman’s Brown-Green-Blue construct, biogenic and inorganic particles play a major role in limiting or stimulating primary production and thus in generating and sustaining hypoxic areas. To better understand processes leading to hypoxia, the sources, settling and sinks of particulate matter must be understood. The major sources of suspended and sinking particles on the Texas-Louisiana Shelf (river plumes, primary production, and resuspended sediments) are all dependent on different processes. The freshwater plume carries organic and inorganic particles from the river onto the shelf, but the particle concentration is too low to increase the fluid density enough to cause the plume to sink. Instead, it spreads out on the surface to an extent that is highly dependent on the volume of river discharge, prevailing winds, and currents
(Hetland, 2005; Zhang et al., 2012). Most of the inorganic and organic particles entering the ocean from rivers flocculate or aggregate and settle to the seafloor as it mixes with seawater, which happens mostly in the lower the river (Meade, 1972). Some of the finest particles remain mixed in the “freshwater” plume that spreads out on the surface (Son et al., 2012). As the plume water mixes with seawater, the particle concentration also decreases by dilution and can sometimes be used as a proxy for plume salinity (Son et al., 2012).

Primary productivity relies on nutrients, which are predominantly supplied by river discharge, with lesser amounts input from wetlands (Bianchi et al., 2002), respired organic matter in the water column, and from seafloor porewaters and fluid mud (Aller, 1998). The other essential input for primary production is light, which is depth limited because of attenuation by water plus terrigenous and biogenic particles in the water. Primary productivity can occur on the shelf down to 20 m and greater, provided nutrients are available and the overlying water is sufficiently clear to allow light to penetrate (Shaeffer et al., 2011). Particles blocking the light could come from the river plume, from biological productivity or bottom sediments resuspended by currents and waves or lateral advection.

**Sampling Approach**

Particle concentrations in the water column can be determined by filtering discrete bottle samples combined with optical sensors that measure light attenuation or scattering to detect the presence of suspended particles (Gardner et al., 2001; Boss et al.,
Discrete bottle sampling and filtration for total Particulate Material (PM) and Particulate Organic Carbon (POC) makes it possible to calibrate the optical instruments for particle concentration and to determine the composition of the material and potentially its generic source. This provides an optical proxy for the concentration of PM and POC in the water at much higher vertical resolution than would be possible by discrete bottle sampling. Size and composition of particles affect optical responses, but they predict PM concentration well with careful calibration (Baker and Lavelle, 1984; Downing, 2006). The magnitude of the optical signal can differ for terrigenous clay particles versus biogenic particles (Baker and Lavelle, 1984; Bunt et al., 1999; Boss et al., 2004; Cetinic et al. 2012). Among biogenic particles, those that contain little carbonate or siliceous skeletal material (e.g. cyanobacteria) yield a smaller signal per unit mass than plankton with skeletal material such as diatoms and coccoliths. Large POC percentages suggest high primary productivity in a given location, while small percentages of POC suggest more riverine input or resuspended sediment in which most carbon has been utilized.

**CDOM**

Colored Dissolved Organic Matter (CDOM) is the fraction of dissolved organic matter (DOM) that absorbs solar radiation, limiting primary productivity by reducing the amount of photosynthetically available radiation (PAR) (Durako et al., 2010). CDOM is a mixture of organic compounds that are decay products of plants and enter the ocean from rivers and wetlands. It is mixed in the freshwater plume with seawater and can be
used as a tracer of salinity along the mixing curve between fresh and salt water since it cannot sink independent of the water (Chen and Gardner, 2004; Chen et al., 2004; Nelson and Siegel, 2002; Coble, 2007; D’Sa and DiMarco, 2009; Shank and Evans, 2011). CDOM is subject to photo-oxidation, so CDOM is not a completely conservative property of sea water (Coble, 2007; Shank and Evans, 2011) and its concentration will decrease over time in sunlight waters. Although the CDOM/salinity correlation will decline, it can be considered well-correlated for the time and space scales investigated within this study.

Other sources of CDOM are marine biological production (phytoplankton, zooplankton, microbial), and sediments (Chen and Gardner, 2004; Chen et al., 2004). Chen and Gardner (2004) and Chen et al. (2004) reported thin bands of CDOM maxima concentrated along iso-pycnals between 16 and 30 m during their northern Gulf cruises in 2000 and 2001. They also reported that mixing from multiple sources, photodegradation, and biological processes make differentiation of the specific sources of CDOM difficult.

CDOM from all sources can be measured with fluorescence sensors tuned to specific wavelengths. The WetLabs sensor (used in this study) is tuned to be more sensitive to terrestrial CDOM than oceanic CDOM (Nelson and Siegel, 2002; Shank and Evans, 2011; Nelson, et al., 2012), but it is not possible to differentiate between these two sources with a single instrument other than by inference from the location and in conjunction with other water properties. CDOM in surface waters is usually associated with fresh-water input. Chen and Gardner (2004) and Chen et al. (2004) concluded that
when CDOM was observed in deeper (10-20 m) higher-salinity water and was spatially associated with elevated chlorophyll fluorescence, this was evidence that in situ primary production had occurred. Therefore, the CDOM present was a product of in situ respiration, not from the plume waters, since CDOM is dissolved. CDOM can only be transferred downward by mixing, not settling. D’Sa and DiMarco (2009) also observed concentrations of CDOM that were above the linear mixing line of fresh river water and open ocean water, and noted those waters frequently had elevated chlorophyll and bacterial counts as well. They argued that the deep CDOM resulted from microbial activity on organic matter, but didn’t state whether the organic matter was produced in situ or had settled after production in surface waters.

**Light Limitation**

Schaffer et al., (2011) show that much of the seafloor of this study area is frequently within the 1% light level, which can be estimated using satellite data. What the satellite may not record accurately in the 8-day averages is the attenuation of light due to changing particle concentrations in the bottom boundary layer. Our study uses in situ CTD- and Acrobat (Sea Sciences Inc. Acrobat)-mounted optical proxy measurements of PM and POC, fluorescence, and PAR as well as CDOM, and CTD data on stratification as evidence for particle sources (plume vs. resuspension vs. productivity). We also evaluate evidence of primary production (chlorophyll $a$ fluorescence (Chl)) and phytoplankton decay (marine CDOM fluorescence in deep,
high-salinity areas unaffected by plume mixing) to determine the role that particles play in affecting conditions that lead to hypoxia.

The goal of this study is to better understand the role of organic and inorganic particles in processes that cause spatial and temporal variability in the intensity and extent of the hypoxic area. POC transfer from surface waters through the thermocline provides an input to subpycnocline waters in addition to respiration of DOC that will lead to oxygen consumption, whereas POC produced through subpycnocline primary production leads to both a source of oxygen in bottom waters and a sink for oxygen when that POC is respired. The amount of oxygen produced during subpycnocline photosynthesis equals the amount of oxygen used during respiration – no net gain or loss, but the timing and rate changes of these processes could influence whether or not water becomes hypoxic. The effects of particle concentration and composition on potential hypoxic areas makes it particularly important to understand the role of PM and POC on the Texas-Louisiana Shelf.

**Hypothesis**

The Brown-Green-Blue model of Rowe and Chapman (2002) is valid for explaining the many of the ecological and physical dynamics of the region in general, but this thesis examines more closely the role of organic and inorganic particulate matter in causing hypoxic conditions along the Texas-Louisiana shelf. The primary hypothesis is:

Organic and inorganic particles are related to dissolved oxygen concentrations.
To answer that hypothesis we propose to address the following guiding questions:

1. Can we calibrate the optical instruments in this complex shelf environment to estimate concentrations of PM (or POC) adequately?
2. Are particles and dissolved oxygen correlated?
3. What is the time scale on which respiration can create hypoxia?
4. Is there sufficient POC in bottom waters to create hypoxia?
5. What is the affect of subpycnocline carbon production on hypoxia?

Study Area

Continuing the annual studies of hypoxia in the Gulf of Mexico carried out by DiMarco and others studying Mechanisms of Coastal Hypoxia (hypoxia.tamu.edu), cruises were made June 25-29 (MS03) and August 9 - 15, 2011 (MS04) aboard the R/V Manta (fig. 3A and B). In 2011 there was a severe drought in Texas, but Texas rivers are a minor component of the Mississippi discharge. The Mississippi and Atchafalaya rivers flooded in 2011 because of abundant rain within their upper drainage basin. Maximum river discharge in 2011 was about twice the average maximum discharge (fig. 4)

Due to weather constraints, the Acrobat was in the water for only six, short cross-shelf lines in June, and five of the June transects were made on the eastern side of the study area, thereby limiting most comparisons of Acrobat transects during the two cruises to the eastern area. Most sampling occurred in water < 30 m except south and east of the Mississippi delta where stations rapidly increased to > 300 m.
Maps of chlorophyll $a$ based on satellite ocean color algorithms were constructed after the cruises using the Giovanni interface (Acker and Leptoukh, 2007) to reveal where our sampling occurred relative to distribution of chlorophyll and other parameters. Maps of 8-day averages of chlorophyll $a$ (fig. 5A and B), which have a logarithmic chlorophyll $a$ scale, show a strong offshore gradient and higher chlorophyll concentrations throughout the area in June than August.

Schaeffer et al. (2011) calculated monthly averages of %PAR reaching the seafloor in our study region based on satellite data from 1998-2007 (fig. 6A and B). Their maps suggest that the offshore (>15-20 m) and western areas (west of 90.5°W in June and west of 92.5°W in August) are more likely to receive light at the seafloor (up to 10% of surface PAR) than areas to the east. The near-shore “hot spots” between 90.5°W and 92.5°W in June and August are topographic highs and thus the seafloor is exposed to more light.
METHODS

Optical instruments were interfaced with the CTD, Acrobat and shipboard flow-through systems to serve as proxies for several parameters of importance in the water column (see table 1). A light sensor was mounted on the top of the CTD to measure Photosynthetically Available Radiation (PAR) on each profile. In order to calibrate optical instruments for particle proxies, bottle samples were taken from the CTD as well as the flow-through system. The CTD bottle samples for total Particulate Matter (PM) and Particulate Organic Carbon (POC) were collected from surface, middle and bottom depths, and concentrations were later regressed against values from a WetLabs FLNTU that measures chlorophyll a fluorescence (Chl) and total backscattering \( b_b \) at 700 nm. The “scale” and “dark” factors provided by the manufacturer were used with the voltage output to obtain chlorophyll a (µg l\(^{-1}\))

\[
\text{Chl} \ a \ (\mu g \ l^{-1}) = \text{Scale Factor} \times (\text{Output} - \text{Dark Counts})
\]

and NTU units

\[
\text{NTU} = \text{Scale Factor} \times (\text{Output} - \text{Dark Counts}).
\]

The conversion from NTU (700 nm, 140 degrees, formazin calibration) to backscattering \( b_b \) is:

\[
b_b \ (m^{-1} \text{ per steradian}) = 0.0025 \times \text{NTU}
\]

(Ian Walsh, WetLabs, personal communication).

CDOM (Quinine Dihydrate Equivalent) concentration, expressed in ppb, was derived in a similar fashion using the equation:
CDOM (QSDE) = Scale Factor * (Output - Dark Counts)

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<tr>
<td>Beam $c_p$ WetLabs Transmissometer PM proxy</td>
<td>Backscatter: 700 nm WetLabs FLNTU (deep) PM proxy</td>
<td>Backscatter: 700 nm WetLabs FLNTU (shallow) PM proxy</td>
</tr>
<tr>
<td>Chlorophyll $a$ fluorescence Chelsea Aquatracker III</td>
<td>Chlorophyll $a$ fluorescence WetLabs FLNTU (deep) 470/695 nm</td>
<td>Chlorophyll $a$ fluorescence WetLabs FLNTU (shallow) 470/695 nm</td>
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<tr>
<td>CDOM fluorescence WetLabs FLCD 370/460 nm</td>
<td>CDOM fluorescence WetLabs FLCD 370/460 nm</td>
<td></td>
</tr>
<tr>
<td>Salinity</td>
<td>Salinity</td>
<td>Salinity</td>
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<tr>
<td>Temperature</td>
<td>Temperature</td>
<td>Temperature</td>
</tr>
<tr>
<td>Dissolved $O_2$</td>
<td>Dissolved $O_2$</td>
<td></td>
</tr>
<tr>
<td>PAR</td>
<td></td>
<td></td>
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<tr>
<td>Discrete samples for lab analysis</td>
<td>Dissolved $O_2$</td>
<td>Dissolved $O_2$</td>
</tr>
<tr>
<td>Nutrients</td>
<td></td>
<td></td>
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<tr>
<td>Particulate Matter</td>
<td>Particulate Matter</td>
<td></td>
</tr>
<tr>
<td>POC</td>
<td>POC</td>
<td></td>
</tr>
</tbody>
</table>

Bottle particle concentrations are minimums because rapidly settling particles will settle to the bottom of Niskin bottles before samples are taken (Gardner, 1977). Because of the configuration of the Niskin bottles on the CTD, it was not possible to collect samples to correct any discrepancy, as is true in virtually all particle sampling programs.

Large aggregates can be broken up in the ship’s seawater flow-through system,
but the mass concentrations should be unaltered. The flow-through concentrations of bulk PM and POC were compared to beam attenuation from an in-line WetLabs C-Star transmissometer (beam attenuation is a linear proxy for particle concentration; Gardner et al., 1993) in order to both calibrate the instrument for particle concentrations of each type, and to compare the composition of the particles collected.

PM concentrations were measured by filtering 100-525 milliliters of seawater through pre-weighed 47 mm wide, 0.4 µm Poretics filters and rinsing them five times with 0.2 µm filtered reverse osmosis (RO) water to remove salt from the filter. Every tenth filter was a treated as a blank, and thus rinsed five times with RO water to account for potential errors in the procedure, such as contamination of RO water and sample handling (Gardner et al., 2001). All filters were immediately dried at low heat (<60°C) onboard the ship, stored in sealed petri dishes and re-weighed onshore. Filters were re-weighed using the same scale and at the same temperature and humidity as their initial weighing.

To measure POC, 70-1050 milliliters of seawater were filtered using pre-combusted 25 mm glass fiber filters (GFF). These samples were not rinsed or dried, but wrapped in pre-combusted aluminum foil and frozen. All POC samples were fumed in a 12M HCl chamber for 24 hours then dried overnight at 50-60 °C. Each sample was folded and inserted into 9 mm tin capsules, and run through a Carlo Erba NA1500 elemental analyzer in the Stable Isotope Geosciences Facility at Texas A&M University.

The filters often overfilled the tin capsules used in the CHN analyzer, resulting in some samples getting stuck in the machine. As a result, about 20% of the POC samples
were lost from June (MS03) samples. A technician attended the samples as they dropped down through the machine for August (MS04) samples, however, about 15% were lost. A few POC samples were below detection levels due to insufficient water being filtered, while a few others exceeded the calibrated range of the elemental analyzer. In August, sampling volumes were adjusted to alleviate this problem; sufficient water was filtered to obtain appropriate coloration on the filter. Results from August show this to be effective, as all filters were within the calibrate range of the POC analyzer and fewer had insufficient material. A few bottom samples on each cruise were discarded where the CTD hit the bottom and resuspended sediment prior to bottle closure (based on the \( b_b \) signal and shipboard observations such as mud on the instrument), giving anomalously high bottom particle concentrations.

To establish a proxy calibration for PM and POC from the optical instruments, PM and POC concentrations from CTD and flow-through samples were regressed against \( b_b \) from the FLNTU on the CTD and against beam attenuation (\( c_p \)) from the shipboard in-line transmissometer (Gardner et al., 1993). The \( b_b \) data (average of 9 measurements) were taken when each Niskin bottle was tripped during stops on the upcast of the CTD, so the data were simultaneously collected from the same volume of water. PM concentrations from the flow-through samples were regressed against simultaneously measured flow-through beam \( c_p \) values. Despite the differences in instrumentation (\( b_b \) (m\(^{-1}\)) vs beam attenuation (m\(^{-1}\))) (Dall’Olmo et al., 2009), a comparison can be successfully made between \( b_b \) and beam \( c_p \) by relating the PM/\( b_b \) and
PM/beam c_p regressions.

The shallow-housing WetLabs FLNTU on the Acrobat and the deep FLNTU on the CTD were both calibrated in the laboratory using sediment from a core top near the Mississippi Canyon so that field data from the two systems could be compared. A watertight vertical cylindrical chamber was constructed with an opening in the top plate that would accommodate either instrument and was sealed by double O-rings. Core-top sediment was prepared by sonic disaggregation, wet sieving at 63 µm, and settling in a graduated cylinder for a calculated time to let all particles > 8 µm in diameter settle below a fixed depth in the standard manner of doing a standard pipette grain size analysis. A sample was then drawn for use in the calibration. The chamber was filled with reverse osmosis water filtered at 0.2 µm and a sample of water was taken to measure baseline particle concentration by filtration through a preweighed Poretics 0.4 µm membrane filter. Instruments were put into the chamber serially for a clean-water reading. A portion of the sediment slurry was poured into the chamber and mixed thoroughly with a perforated mixing plunger, after which one instrument was put into the chamber for a reading. The water was again thoroughly mixed and a reading from the other instrument was made. A sample was immediately drawn from the water and filtered through Poretics filters for mass concentration. A total of ten concentration measurements were made for calibration in this manner.

Although the CTD and Acrobat had deep and shallow models respectively of the FLNTU instrument, their optics configurations were identical. The laboratory calibration of both instruments yielded a linear response to the <8 µm sediment collected from the
study area (fig. 7A and B) \( r^2 = 0.996 \) in both cases), but the slope of the two linear regressions differed by about 10% (fig. 7B). The purpose of the intercomparison was to normalize the Acrobat \( b_b \) values to the CTD \( b_b \) values because we were only able to collect field samples for in situ calibration from the CTD. The intercalibration provided evidence that the two instruments give a linear concentration response to a given set of particles that are partially representative of our field area. The calibrations that were applied to obtain PM in figures used the in situ samples obtained during the each cruise, not the laboratory calibrations.

Before converting the Acrobat \( b_b \) values to PM concentrations, the Acrobat \( b_b \) was converted from the CTD \( b_b \) using the equation \( b_b(2276) = 1.117 \times b_b(967) - 0.976 \) (fig. 7B). PM concentrations were then determined from the combined mid and bottom sample concentrations versus \( b_b \) for each cruise separately. Of course, in graphing the Acrobat PM concentrations in surface waters the sections use the same PM vs \( b_b \) relationship in surface waters, though the calibration is not the same. It was not practical to separate surface from mid/bottom waters along the sections. Concentrations in surface waters are actually about 10% higher than the scale would indicate (fig. 7).

The Acrobat undulated from 1-2 m below the sea surface to 1-2 m above the seafloor as it was towed behind the ship, measuring temperature, salinity, dissolved oxygen, CDOM fluorescence, chlorophyll \( a \) fluorescence, and \( b_b \) comparable to the CTD. The Acrobat data has the advantage of high vertical and horizontal resolution (~200 m) along transects between CTD stations. These data were examined for
relationships among $b_b$, chlorophyll $a$ fluorescence, CDOM fluorescence, salinity, density and $O_2$ to give a more detailed view of the property distributions that could provide evidence of the physical processes taking place. The Acrobat transects were run perpendicular to the coast at frequent intervals along the Texas-Louisiana Shelf to the Mississippi River delta (fig. 3A and B).
RESULTS AND DISCUSSION

**Optical Proxy Validation for PM and POC**

In order to achieve the goals of this work, it was necessary to calibrate the optical measurements so we could determine the distribution of particulate matter in this shelf region. After plotting PM (or POC) concentration versus $b_b$ (figs. 8-10) we calculated a linear least squares regression to estimate PM from $b_b$. Because surface-water particles are typically richer in biogenic particles than in mid and bottom waters, and bottom waters often include resuspended sediment (Gardner, 1989; Gardner et al., 2001; Holser et al., 2012; Boss et al., 2009), we divided samples into surface, mid, and bottom waters for each cruise separately based on hydrographic and optical parameters (e.g. surface and bottom mixed layers). When the bottles were closed in surface waters during the upcast there were sometimes bubbles being generated by the jets of the ship propulsion system (as seen in video from a camera mounted on the CTD). These bubbles could elevate the readings of $b_b$ substantially, and fluorescence to a lesser degree. This required careful examination of each surface $b_b$ value to be sure they were not bubble contaminated, as evidenced by high $b_b$ variability at constant depth on station.

The bottom and mid water PM for both cruises were well correlated with $b_b$ (see table 2) with $r^2$ values of 0.87-0.93 in bottom waters, and 0.90 – 0.94 in mid waters. The mid and bottom waters were sufficiently similar that we combined them into a single regression for each cruise to make one equation to convert $b_b$ to PM below surface...
waters for the Acrobat sections (fig. 11). For maps of bottom PM we used just the regression from bottom samples. There was more scatter in the surface water for August (MS04) PM because of one point near the Mississippi outflow. When that point was removed, $r^2$ in surface waters for both cruises was 0.87-0.94. The regression slope was smaller in surface than mid or bottom waters, suggesting a different composition and/or size of the particles (Baker and Lavelle, 1984).

**Table 2. PM vs. $b_b$ (PM vs. $c_p$) combined for both cruises.**

<table>
<thead>
<tr>
<th></th>
<th>Slope</th>
<th>Intercept</th>
<th>$R^2$</th>
<th>P</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>June</td>
<td>Surface</td>
<td>0.78</td>
<td>-3.05</td>
<td>0.87</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>0.78</td>
<td>-2.75</td>
<td>0.93</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>1.10</td>
<td>-5.17</td>
<td>0.88</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Mid &amp; Bot</td>
<td>0.99</td>
<td>-4.11</td>
<td>0.89</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>August</td>
<td>Surface</td>
<td>0.80</td>
<td>-2.14</td>
<td>0.64</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>1.00</td>
<td>-3.65</td>
<td>0.94</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>1.24</td>
<td>-5.35</td>
<td>0.91</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Mid &amp; Bot</td>
<td>1.18</td>
<td>-4.79</td>
<td>0.92</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>June &amp; August</td>
<td>*Flowthrough</td>
<td>1.40</td>
<td>0.15</td>
<td>0.96</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

Good correlations have been measured between POC and $c_p$ in other regions (Gardner et al., 1989; Stramski et al., 2008; Son et al., 2009) and between POC and $b_p$ - the backscatter due only to particles (Cetinic et al., 2012; Boss et al., 2009). Our POC correlations were strong, but had lower correlations than with PM (see table 3), which is consistent with previous studies cited above. There was a strong correlation in both mid (usually subpycnocline) and bottom waters, often with similar slopes, which is not
surprising since water depth for most stations was <30 m, often making it difficult to separate the water column into three distinct zones. This suggests that the subpycnocline particulate matter composition and size distributions were more uniform than we expected and allowed us to use a single regression to estimate subpycnocline POC concentrations.

<table>
<thead>
<tr>
<th></th>
<th>Slope</th>
<th>Intercept</th>
<th>R²</th>
<th>P</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>June</td>
<td>Surface</td>
<td>0.213</td>
<td>-0.845</td>
<td>0.72</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>0.147</td>
<td>-0.501</td>
<td>0.75</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>0.234</td>
<td>-1.299</td>
<td>0.92</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Mid &amp; Bot</td>
<td>0.196</td>
<td>-0.822</td>
<td>0.88</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>*Flowthrough</td>
<td>0.462</td>
<td>-0.083</td>
<td>0.90</td>
<td>&lt;0.004</td>
<td>6</td>
</tr>
<tr>
<td>August</td>
<td>Surface</td>
<td>0.118</td>
<td>-0.342</td>
<td>0.52</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>0.081</td>
<td>-0.296</td>
<td>0.84</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>0.126</td>
<td>-0.625</td>
<td>0.88</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td></td>
<td>Mid &amp; Bot</td>
<td>0.117</td>
<td>-0.463</td>
<td>0.69</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>*Flowthrough</td>
<td>0.123</td>
<td>-0.013</td>
<td>0.97</td>
<td>&lt;0.003</td>
<td>5</td>
</tr>
</tbody>
</table>

Flowthrough PM and POC Calibrations

Flowthrough PM vs. c_p had a strong correlation, though there were far fewer data in the regression of those data than from the CTD profiles. All flow-through calibration sampling was done in surface water. Measurements for PM were combined for June and August because relatively few samples were available and they followed the same trend (fig. 12). Similar measurements were made for POC and c_p, but the slopes of the regressions were different in June versus August, so separate regressions were used for
June and August. Similar calibrations for surface waters have been made in New England shelf waters and the slope of the PM and POC correlations were similar to those in the northern Gulf of Mexico (Gardner et al., 2001).

**Property Distributions Along Shelf: Surface Mapping**

At the beginning of each cruise, a line of CTD stations was made from the west (~Galveston) to the east of the study area (89.5 °W in June and 90 °W in August) (figs. 3, 13, 14) to survey the general distribution of properties such as temperature, salinity, PM (from the beam attenuation proxy for particles), and CDOM. Surface temperature was quite uniform across the area during both cruises, but was about 2°C warmer in August than June (figs. 13, 14). Salinity was lowest near the Mississippi outflow (17-22) and rose above 26 by 90.5 °W in June and by 91.5 °W in August. Salinity was much more variable west of 91°W during June and reached a maximum of only 33 in June, and 36 in August.

As noted earlier, rivers and wetlands are the primary sources of surface CDOM, so CDOM can be used to trace freshwater mixing (Nelson and Siegel 2002; Chen and Gardner, 2004; Chen et al., 2004; Coble, 2007; D’Sa and DiMarco, 2009; Shank and Evans, 2011). The inverse correlation between salinity and CDOM in this study is linear (fig. 15), with 5-10 ppb more CDOM in June than August for the same salinity, suggesting higher concentrations of CDOM coming from rivers in June. A map of surface CDOM along each entire cruise track showed highest concentrations near the Mississippi outflow and near the coast, including near Galveston Bay (fig. 16), with
decreasing concentrations offshore and to the west during both cruises. Higher CDOM concentrations during June are apparent from these maps.

Maps of surface values of PM (from flowthrough beam attenuation) during each cruise showed PM was high near the Mississippi outflow during both cruises, decreased westward, and increased substantially near the coasts and Galveston Bay (fig. 17). Rivers are an obvious source of particles near the Mississippi River plume and Atchafalaya Bay. On the western shelf the increase in particles could come from local resuspension, from sediment resuspended along the coast and carried in the coastal current, or from primary production of particles. Winds during June were strongly downwelling favorable (easterly and southerly) but shifted to downwelling favorable (westerly and northerly) from early July to mid August (S.F. DiMarco, personal communication). Winds were stronger during the June cruise than the August cruise, which would have enhanced coastal resuspension of bottom sediments and full water-column mixing in shallow areas.

**Bottom PM and POC Distribution**

PM concentrations in bottom waters (converted from CTD $b_b$ values) were low south of the Mississippi delta, but increased westward along the shelf (fig. 18). Concentrations were generally higher nearshore, as expected. Particle concentrations were higher in June than August, which could have resulted from stronger winds and waves resuspending bottom sediments (see table 4).
Table 4. Mean PM concentrations in Surface, Middle and Bottom waters from all stations sampled.

<table>
<thead>
<tr>
<th></th>
<th>PM Concentrations (mg l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>June</td>
</tr>
<tr>
<td>Surface</td>
<td>2.90</td>
</tr>
<tr>
<td>Middle</td>
<td>1.68</td>
</tr>
<tr>
<td>Bottom</td>
<td>6.99</td>
</tr>
</tbody>
</table>

POC concentrations in bottom waters (fig. 19), based on the $b_b$ values at the bottom of each CTD profile using the calibration shown in figures 9 and 10, show a similar pattern as for PM. This provides a sense of overall bottom concentrations that will be further analyzed below.

POC, %POC, and C:N Ratios Along the Shelf

POC was measured to determine the amount and percentage of PM that was organic material. These bulk measurements provide evidence about whether the particles are predominantly biogenic in origin (high %POC), river outflow, or resuspended from the seafloor (low %POC).

Surface water POC concentrations were higher in June than August and decreased westward in both months (data not shown). A plot of POC concentration in mid and bottom waters versus longitude along the shelf revealed no clear spatial trends in midwater during either cruise, nor in comparisons between cruises (fig. 20). In bottom waters, POC concentrations were more variable in June than in August. On both cruises,
near-shore stations typically had a higher %POC than the matching offshore station (data not differentiated in fig. 20). Hypoxic stations had both high and low POC.

The percentage of POC in surface water particulate matter ranged from 3-42% during June and 3-25% in August with mean values being nearly twice as high in June than August (see table 5). A westward decrease in %POC in surface waters occurred in both June and August (fig. 21). In midwater the percentage increased westward from 6% to 33% in June, but in August the range was only 4-13% with no east-west trend. Bottom-water percentages were more variable in June (5-32%) than in August (4-17%) with insufficient data to show any significant east-west trend. The larger variability in June stands out in the large differences in standard error (StError) for %POC, with June StError being 3-5 times larger than the August StError at all three depths. (see table 5)

### Table 5. Percentage of PM that is POC across shelf.

<table>
<thead>
<tr>
<th></th>
<th>%POC</th>
<th>STError</th>
<th>%POC</th>
<th>STError</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>20.0</td>
<td>3.05</td>
<td>12.2</td>
<td>1.15</td>
</tr>
<tr>
<td>Middle</td>
<td>14.5</td>
<td>2.73</td>
<td>7.0</td>
<td>0.52</td>
</tr>
<tr>
<td>Bottom</td>
<td>17.0</td>
<td>3.11</td>
<td>8.7</td>
<td>0.80</td>
</tr>
</tbody>
</table>

The C:N ratio was lower in June than August in the three depth zones (see table 6), but there is no clear spatial trend in the data other than a slight westward increase in bottom C:N (fig. 22).
Table 6. C:N ratios across shelf.

<table>
<thead>
<tr>
<th></th>
<th>C:N Ratio</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>June</td>
<td>STError</td>
<td>August</td>
</tr>
<tr>
<td>Surface</td>
<td>6.3</td>
<td>0.249</td>
<td>7.8</td>
</tr>
<tr>
<td>Middle</td>
<td>5.8</td>
<td>0.201</td>
<td>7.8</td>
</tr>
<tr>
<td>Bottom</td>
<td>6.1</td>
<td>0.312</td>
<td>8.5</td>
</tr>
</tbody>
</table>

The higher concentrations and %POC in surface waters in June than August suggest higher biomass from productivity in surface waters in June, which is consistent with the June Mississippi discharge being at near record levels (fig. 4). The organic matter showed higher C:N ratios in August, consistent with greater diagenetic alteration of organic matter by August than in June. The concentration and percentage of POC tended to decrease westward in surface and bottom waters, but in midwater there was a westward increase in both concentration and %POC in June. A westward midwater increase could result from greater surface productivity and particle settling or greater subpycnocline in situ productivity. Given the low surface Chl in CTD profiles and Acrobat sections, subpycnocline productivity seems more likely.

The %POC is usually higher at near-shore stations in both surface and bottom waters all along the shelf, suggesting higher productivity near shore – at least shoreward to the 10 m isobath where our sampling ended. These trends are all consistent with the greater Chl observed nearshore from satellite data (fig. 5).
**River Discharge**

Although there was a severe drought in Texas during summer 2011, Texas represents only a small portion of the total freshwater volume to the NGM. Outflow from the Mississippi and Atchafalaya Rivers was well above normal in 2011 because of the heavy rainfall in the upper drainage basin (fig. 4). Discharge peaked in mid May at about twice the 7-year median and was well above the 7-year median during both of our cruises. Discharge in August was about half that in June, so it is probable that fewer nutrients were available in August, which is consistent with the lower POC concentrations in August. Note that river flow was measured at Baton Rouge, LA, so the large outflow experienced at the mouth of the Mississippi and Atchafalaya Rivers and along the study area occurred later than at Baton Rouge. Baton Rouge is 367 km (228 miles) from the Mississippi River mouth, but at an average river speed of 4.8 km/hr (3 miles per hour) (http://www.nps.gov/miss/riverfacts.htm), it required only 3.2 days to move to the river mouth.

**Hypoxia in June and August**

Using oxygen data from both the CTD and Acrobat transects, DiMarco et al. (2012) mapped the distribution of dissolved oxygen in bottom waters and calculated the area meeting the hypoxic criteria of $< 1.4 \text{ ml} \text{l}^{-1}$ (fig. 23). Although the total area experiencing hypoxic water was similar at both times (June - 8445 km$^2$; August - 8772 km$^2$), the range of hypoxic area was much greater in June than August (June - 3650 to 16018 km$^2$; August - 8336 to 9644 km$^2$) based on optimal interpolation and objective
analysis. Bottom waters in June had more area that was near hypoxic levels than in August. Hypoxic areas also existed further to the west in June than August.

There was no obvious overall correlation between bottom PM or POC concentration and areas of hypoxia from CTD data (compare figs. 18, 19, 23). This was quantified by plotting PM versus O₂ and calculating linear regressions. All regressions had r² values of < 0.2 (not shown). We also plotted b₀ (proxy for PM) versus O₂ at all depths along a few Acrobat sections. Most of them showed correlations that were difficult to interpret, but Acrobat line 16 data were divided into five density bins for further evaluation (fig. 24). Surface values (s_T>7.5) were high for both parameters, then decreased in mid waters (s_T =7.5-17.5) for both parameters. In the hypoxic layer at about 10 m (s_T =17.5-22.5), O₂ decreased as PM increased. The near-bottom water (s_T >23) had elevated PM concentrations, but slightly higher O₂ concentrations, bordering on hypoxia. To better understand the time scale on which oxygen utilization occurs, we calculated the time required to respire enough oxygen to turn the water hypoxic and calculated whether or not there was enough POC in bottom waters to utilize the O₂ in mid and bottom waters.

**Oxygen Utilization and POC Respiration**

The Acrobat tows across the shelf showed that typical subpynnocline waters had oxygen concentrations of about 4 ml l⁻¹. Since waters are classified as hypoxic below 1.4 ml l⁻¹, this requires a utilization of 2.6 ml l⁻¹ O₂ between typical subpynnocline water and hypoxic water. Murrell and Lehrter (2010) reported an average subpynnocline water-
column respiration rate in the northern Gulf of Mexico of 6.8 mmol O$_2$ m$^{-3}$ day$^{-1}$ (± 0.7; std error) and a total respiration rate (including sediment oxygen consumption) of 8.2 mmol O$_2$ m$^{-3}$ day$^{-1}$ (± 0.8; std error). They noted that their measured values fell between the average water-column respiration rates for worldwide compilations of estuarine systems (19.6 ± 3.9 mmol O$_2$ m$^{-3}$ day$^{-1}$: Hopkinson and Smith, 2005) and marine surface water (3.3 ± 0.15 mmol O$_2$ m$^{-3}$ day$^{-1}$: Robinson and Williams, 2005). Using Murrell and Lehrter’s (2010) respiration rate of 8.2 ± 0.8 mmol O$_2$ m$^{-3}$ day$^{-1}$, it would take 14.2 ± 1.2 days to oxidize the 2.6 ml$^{-1}$ of oxygen (116.1 mmol O$_2$ m$^{-3}$) for the average subpycnocline waters to become hypoxic.

Degradation of particulate organic carbon is given by the equation:

$$C_\beta H_\xi O_\phi N_\alpha P + \gamma O_2 = H_3PO_4 + \alpha HNO_3 + \beta CO_2 + \gamma H_2O$$

(1)

where the coefficients $\alpha$, $\beta$, and $\gamma$ are the Redfield ratios. (Feely et al., 2002). The ratios of P/N/Corg/O$_2$, (1/$\alpha$/$\beta$/$\gamma$ in equation (1)) are 1/16/106/138 for idealized marine plankton (Li and Peng, 2002). In order to calculate how much organic carbon must be respired to utilize 2.6 ml$^{-1}$ of oxygen, the C:O Redfield ratio of 106:138 is used (Li and Peng, 2002). Using this ratio, 1.07 mg l$^{-1}$ of organic carbon must be respired to transition from sub-pycnocline O$_2$ concentrations to hypoxic oxygen concentrations. Was there sufficient POC in the water column to utilize enough oxygen to decrease to hypoxic levels?

POC bottle concentrations ranged from (0.006-3.792 mg l$^{-1}$) in water samples from the surface to near the bottom across the Louisiana continental shelf. The averaged POC concentrations at near-bottom (within ~1 m) and mid-water depths across the
Texas-Louisiana Shelf were tabulated (see table 7). The average middle and bottom values in June (0.68 ± 0.23 mg l⁻¹) and August (0.33 ± 0.09 mg l⁻¹) in table 7 was ~0.5 mg l⁻¹. While there are locations where there is sufficient POC to utilize enough oxygen to cause hypoxia, on average there was only about 50% of the POC needed. On average it would take half of 14.2 days, or about 7 days, to utilize all the POC in bottom and mid waters.

If we consider the amount of POC in the bottom water in June (1.27 ± 0.52 mg l⁻¹) and August (0.54 ± 0.17 mg l⁻¹), there was on average more than sufficient POC to utilize 2.6 ml l⁻¹ O₂ to cause hypoxia in June, but still only half the POC needed to reduce bottom waters to hypoxic levels in August. In June, on average, the bottom waters could be turned hypoxic in ~14 days with 0.2 mg l⁻¹ POC remaining and in August, the POC would all be utilized after ~7 days.

Table 7. POC concentrations (mg l⁻¹) across the Texas-Louisiana Shelf.

<table>
<thead>
<tr>
<th></th>
<th>POC Concentrations (mg l⁻¹)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>June</td>
<td>STError</td>
<td>August</td>
</tr>
<tr>
<td>Surface</td>
<td>0.83</td>
<td>0.31</td>
<td>0.40</td>
</tr>
<tr>
<td>Middle</td>
<td>0.32</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td>Bottom</td>
<td>1.27</td>
<td>0.52</td>
<td>0.54</td>
</tr>
<tr>
<td>Middle &amp; Bottom</td>
<td>0.68*</td>
<td>0.23</td>
<td>0.33*</td>
</tr>
</tbody>
</table>

Under non-steady state conditions of POC concentrations, it is likely that more POC was available prior to our sampling and was utilized to create the hypoxic conditions observed with the POC concentration we measured being available for further
utilization of O₂. Under steady-state conditions the lack of sufficient POC in bottom waters suggests there must be other sources of carbon available to utilize oxygen. One such source is dissolved organic carbon (DOC). For POC to be respired by microbial activity, it must first be converted into DOC (Rowe and Deming, 2011). Shank and Evans (2011) reported DOC concentrations of 1-3 mg l⁻¹ in areas from the Mississippi River to west of Atchafalaya Bay. DOC alone could provide enough carbon to create hypoxic bottom waters if all, or most, of the DOC was labile. However, this is outside the scope of my work.

Another source of organic carbon to subpynnocline waters was carbon flux from surface waters. Redalje et al., (1994) measured carbon fluxes from surface waters at 15 m (~30 m water depth) using surface-tethered, free-floating cylindrical traps for 1-2 day periods in the area of our study between 89° and 90.5° W. During July-September, fluxes averaged 290 to 690 mgC m⁻² d⁻¹ in plume waters (n=15) and 180-190 mgC m⁻² d⁻¹ outside the plume on the shelf (n=10). Fluxes were even higher in March and May: 950-1800 mgC m⁻² d⁻¹ in the plume (n=15) and 320-400 mgC m⁻² d⁻¹ on the shelf outside the plume (n=13).

The carbon fluxes measured using floating traps were comparable to the average of 468 ± 256 mgC m⁻² d⁻¹ measured during two three-month summer deployments of moored cylindrical sediment traps at four sites (20-27 m depth) at about the same depth as the floating traps (13-21 m) along 90.5° and 92°W (data calculated from Zhang, 1997). Carbon fluxes south of the plume area at 50 m depth during the same period along 90.5° and 92°W were 168 ± 108 mgC m⁻² d⁻¹. If 500 mgC m⁻² d⁻¹ carbon settles
into the bottom 10 m of the water column (one liter = 1 cm$^2 \times 1000$ cm), it is equivalent to a daily carbon addition of 0.05 mgC l$^{-1}$, which is about 10% of the average amount of carbon we measured in the bottom water column (0.5 mg l$^{-1}$). Therefore, under steady-state fluxes, within 10 days there will be sufficient POC to utilize enough oxygen to make the water hypoxic. Combined with DOC there is more than enough carbon to turn subpycnocline water hypoxic. Carbon fluxes were likely to be much lower in Blue waters due to diminished surface production.

Once enough oxygen is used to cause hypoxia, no further input of POC or DOC is needed to keep waters hypoxic unless there is a renewal of oxygen by mixing with water with higher levels of oxygen or some other source of oxygen exists, such as primary production in bottom or subpycnocline waters. Chen and Gardner (2004) and Chen et al. (2004) noted that when CDOM is observed in higher salinity subpycnocline water in association with elevated chlorophyll fluorescence, it was evidence that in situ primary production had occurred. Elevated chlorophyll fluorescence has been observed beneath Blue waters (D’Sa and DiMarco, 2009; Quigg et al. in prep.) and it was frequently observed beneath Blue waters during our June and August cruises. We have no data on the rate or magnitude of primary production in those subpycnocline waters containing chlorophyll. Assuming subpycnocline production occurs, it is possible that fresh phytoplankton may be converted to DOC and respired more rapidly than refractory components of DOC.

Time series measurements along the Texas coast demonstrated that hypoxic events could be short-lived, lasting 18 – 36 hours (Mullins et al., 2011). This is the time
that the oxygen concentration is < 1.4 ml l\(^{-1}\), not the time required to reduce oxygen from typical subpycnocline values, but it suggests that changes can occur on daily time scales. Whether the hypoxic waters gain enough oxygen to exceed 1.4 ml l\(^{-1}\) from mixing with other subpycnocline waters with higher oxygen or from subpycnocline primary production is unknown and subject to further research.

During June, bottom hypoxic waters usually had higher POC values (fig. 20) and lower subpycnocline oxygen values than in August (fig. 23). Out of the three hypoxic locations that there were POC values for, there was greater than 2 mg l\(^{-1}\) of POC. If one assumed that only POC was being respired, these areas might have started with a greater POC concentration or experienced a greater POC flux – the non-steady state condition.

During August, all hypoxic middle and bottom waters had less than 1 mg l\(^{-1}\) POC and most were under 0.5 mg l\(^{-1}\). There was no systematic difference in POC values between hypoxic and non-hypoxic areas. This suggests that the hypoxic areas have been hypoxic for long enough periods of time to allow POC concentrations to return to normal through either carbon flux from upper waters or in situ production of organic matter.

The time required for surface particles to settle to the seafloor (20 m in much of our area) varies widely based on size and density of particles. Individual plankton cells could take days to weeks to settle, but most particulate matter settles as aggregates or in fecal pellets formed by zooplankton. Settling velocity for fecal pellets can range from 0.14 – 3.6 m hr\(^{-1}\) (Turner, 1977), so they could easily settle 20 m in less than a day.
Brown, Green, and Blue Waters

As a guideline to identifying Brown, Green, and Blue areas of the Rowe and Chapman (2002) model, we constructed a matrix that lists the primary properties determined along the Acrobat transects and provide their relative values in surface and bottom waters for the August period (see table 8). Based on the properties in table 8, we found that the Acrobat line most similar to Brown water conditions was line 16 (fig. 3). Green waters were found along lines 12-15, and the remaining transects were in Blue waters. Some of the lines started in Green water nearshore and terminated offshore in Blue water.

Table 8. Matrix of primary properties for August, 2011.

<table>
<thead>
<tr>
<th>Transsects</th>
<th>Water type</th>
<th>Salinity</th>
<th>Chl from Primary Production (PP)</th>
<th>Turbidity</th>
<th>Bottom-surface Nutrients</th>
<th>CTD 142 = 14.3</th>
<th>River carbon input and marine PP</th>
<th>River CDOM</th>
<th>Marine CDOM</th>
<th>Hypoxia</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Brown-river</td>
<td>Low</td>
<td>High</td>
<td>Low to high</td>
<td>Lower than river plume, bottom respiration</td>
<td>Medium</td>
<td>Very low</td>
<td>High</td>
<td>Very low</td>
<td>None</td>
</tr>
<tr>
<td>12-15</td>
<td>Green</td>
<td>Low, increasing</td>
<td>Medium, decreasing</td>
<td>Medium, decreasing</td>
<td>Medium, decreasing</td>
<td>Patchy</td>
<td>Medium-high, decreasing</td>
<td>Very low</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>3-11</td>
<td>Blue &amp; green</td>
<td>Higher</td>
<td>Very low</td>
<td>Very low</td>
<td>Subproweather PP starts, R</td>
<td>Left</td>
<td>Low, increasing Patchy</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>

In August, Green waters extended only to about 91°W (line 11). West of 91°W was Blue water, which covered both the outer shelf where plume waters seldom penetrate, and the shelf westward where nutrients had been depleted in surface waters, so surface primary production is minor, and both Chl and total particle concentrations were low. This was also near where surface salinity increased rapidly and surface CDOM became minimal, evidence that the Blue water was outside the influence of the river.
plume. Boundaries between waters were usually gradual and irregular because of variability in plume mixing as exemplified in figure 25.

Three representative plots of the parameters measured with the CTD and integrated instruments (Chl, PM (b), Oxygen, Salinity, Temperature, and PAR) in Brown, Green and Blue waters clearly demonstrate the differences among different water types (fig. 26). The location of each profile can be found in figure 3. Station 162 near the Mississippi outflow shows high Chl, PM, and low salinity in the upper 10 m and is the CTD profile closest in characteristics to Brown water. Chl decreases to background levels at depth, but PM increases toward the bottom, salinity is high (>36) and no hypoxia is observed. As a measure of stratification, the density difference between surface and bottom waters is 14.5.

At station 142 (Green waters), Chl is maximum at the surface, but Chl and PM decreased substantially from station 162, salinity is relatively low, layers of nearly hypoxic waters are found at 17 and 37 m, and PM increases near bottom while salinity remains >36 in the lower half of the water column. The density difference between surface and bottom waters is 13.3.

Station L082 is typical of Blue waters where Chl and PM are low in the upper water column, surface salinity is considerably higher than the two previous stations (little plume influence) and oxygen decreases in the bottom mixed layer whereas Chl and PM increase. The density difference between surface and bottom waters is 5.0.

In many of the Blue-type waters, we find that while Chl is low in the surface, Chl increases below the pycnocline with increasing bottom concentrations towards the west.
CDOM also starts to appear (4-5 mg m\(^{-3}\); see following section on Acrobat transects) in the deep areas where fluorescence is high (2-3 mg m\(^{-3}\)). One might speculate that the phytoplankton are settling and fluorescing in bottom waters, but there is no Chl in upper waters as a source. Then the question arises of whether there are sufficient nutrients and light at depth to sustain primary production. And what is the source of CDOM (a dissolved substance usually associated with river runoff in surface waters) in these high-salinity bottom waters? We will argue that there is sufficient light for production, and agree with Chen and Gardner (2004) and Chen et al., (2004), that the CDOM is an in situ decay product of phytoplankton produced in situ below the pycnocline and we refer to this CDOM as “marine CDOM” as opposed to “river CDOM”. Chen et al., (2004) also reported that mixing of water from multiple CDOM sources, photodegradation, and biological processes make differentiation of the specific source of a CDOM sample difficult.

**PAR Below the Pycnocline**

Is there sufficient light for photosynthesis at these depths given the particle load in the water? Algorithms using MODIS satellite provide estimates of the depth to which 1% of surface light should be able to penetrate in the ocean – the euphotic depth. Maps of euphotic depth during an 8-day period that most closely overlaps the June and August cruises indicate that the euphotic zone should reach the sub-pycnocline waters in the offshore stations in most of the area with a greater area receiving sufficient light in August than June (fig. 27). Schaeffer et al., (2011) showed that large areas of the shelf
west of 90°W received some light at the seafloor during June and August (fig. 6).

To estimate whether or not there is sufficient light for benthic primary production, absolute radiation values are required, not just the percent of surface PAR. Gattuso et al., (2006) reviewed measurements of benthic primary production on global continental shelves. In their table 7, they estimate the minimum light needed for primary production is 2.8 µmole photons m\(^{-2}\) s\(^{-1}\), though they state that this is likely species dependent. We examined the CTD PAR data we collected during daylight hours to see where we exceeded 2.8 µmole photons m\(^{-2}\) s\(^{-1}\) to estimate whether there was sufficient light for benthic production in our study area. A caveat is that CTD profiles were taken around the clock, so ~75% of the profiles were not taken in full sunlight, causing an absence of light at station bottoms that is not the result of low light attenuation.

The stations where light exceeded 2.8 µmole photons m\(^{-2}\) s\(^{-1}\) at the seafloor during June were limited to two stations east of the MS delta (E32 and E51, fig. 3), and six stations west of 92.5 °W (LA11, A11, LA15, LO32, L011, L012). Sixteen more stations exceeded 2.8 µmole photons m\(^{-2}\) s\(^{-1}\) at 10 m, which was usually in subpycnocline waters, so water column production was possible in addition to seafloor production. The situation was similar in August with >2.8 µmole photons m\(^{-2}\) s\(^{-1}\) at nine stations (A14, A15, L032, L042, L052, L081, L102, L112, and LA10. Eleven more stations exceeded 2.8 µmole photons m\(^{-2}\) s\(^{-1}\) at 10 m depth (fig. 3). Thus, our in situ data confirm that there were times and many locations where there was sufficient light in subpycnocline waters for primary production.
Nutrients, Chlorophyll, PM and Hypoxia

Nutrients are essential for primary production. If production occurs in surface waters, the organic matter can settle through the pycnocline, thus utilizing oxygen below the pycnocline through respiration. Conversely, if there are nutrients below the pycnocline and sunlight is able to penetrate to those depths, primary production can also occur beneath the pycnocline and prevent hypoxia by producing oxygen. If the particle loading becomes sufficient to block the light, phytoplankton production will slow and eventually cease, leaving fresh organic matter for oxygen utilization. We mapped and compared the abundance of bottom PM (fig. 18), nitrate (fig. 28), DIN (fig. 29), Chl (fig. 30), and hypoxia (fig. 23), and found that hypoxia can occur in areas with either high or low nitrate. During June, hypoxic stations with > 10 µM NO₃ were A03, A04, L141 and L161. Hypoxic stations with < 1 µM NO₃ were L131, L131, and L151. During August, hypoxic stations with > 10 µM NO₃ were A01, A02, LA02 and L132. Hypoxic stations with < 1 µM NO₃ were LA04, LA11, L091 and L131.

Quigg et al., (2011) studied the role of dissolved inorganic nitrogen (DIN = NO₃⁻ + NO₂⁻ + NH₄⁺), phosphate, silica and light in limiting primary production in surface waters at stations between the Mississippi outflow and the Atchafalaya outflow (westernmost station at 92°W). While they did not state a specific concentration below which DIN was limiting, they did state that strongest nitrate limitation was recorded in the equivalent of blue waters collected off the coast of the Atchafalaya River, which had
a salinity of 32, and low concentrations of DIN and inorganic phosphorous (<0.1 µM for both). They stated that nitrogen limitation was generally observed at stations offshore and west of the Atchafalaya River.

Landry et al., (1998) found that primary production in the open ocean becomes limited when nitrate is below 0.5 µM. Dufour and Berland, (1999) and Dufour et al., (1999) studied nutrient control of phytoplanktonic biomass in atoll lagoons and Pacific ocean waters and found that optimum concentrations for most phytoplankton species were DIN> 1µM, PO₄> 0.2 µM, and for diatom species, they required SiO₂> 1.5 µM. Because Quigg et al., (2011) did not identify a specific threshold for N-limitation, we chose to use the value of 0.5 µM in identifying areas that might be nitrate limited, and DIN < 1µM for sub-optimal phytoplankton growth. Nitrate in surface waters was < 0.5 µM starting at 90°W in June and 89.5° W in August (fig. 28). Waters with < 0.5 µM nitrate extended over most of the area to the west except along the coast with slightly higher coastal values in June than August. After adding both nitrite and ammonium to nitrate to obtain DIN, the distributions of DIN and nitrate are quite similar in surface waters during both June and August, but there are fewer stations where DIN is < 1µM than where nitrate was < 0.5 µM (fig. 30A and C)

Nitrate in bottom waters remained above 5 µM to at least 90.5 °W in June and was then patchy, but <0.5 µM along the coast (fig. 28C). In August, bottom nitrate was typically <0.5 µM west of 92 °W. During both months there were many stations (11 in June and 18 in August) where bottom nitrate was <0.5 µM, but many stations (23 in June and 21 in August) where it was > 2-3 µM, especially at offshore sites.
The distribution on DIN in bottom waters differed substantially from nitrate because there was abundant nitrite and ammonium in bottom waters in the vicinity of both the Mississippi and Atchafalaya outflows (fig. 29B and D). There were no stations where DIN was <1µM in bottom waters during June and only 10 stations (of 51) in August. Only one station had sub-optimal P concentrations (<0.2µM) in bottom waters in June and only five stations in August. No stations had sub-optimal Si concentrations (<1.5µM) anywhere in the water column in June and only two stations had sub-optimal Si concentrations in mid or surface waters in August.

We hypothesized earlier that the bottom nitrate (or DIN) fueled subpycnocline primary production. Our data show that there was sufficient light and nitrate (or DIN) to support such production in some areas. Is there evidence of Chl production? Figure 30 shows Chl concentrations <1 mg m\(^{-3}\) in bottom waters east of 90.5 °W, but concentrations were frequently > 2-5 mg m\(^{-3}\) west of 90.5 °W. The Acrobat transects often showed high Chl near the bottom and a corresponding high CDOM, indicative of production and subsequent degradation of phytoplankton as investigated by Chen et al., (2004).

If we compare the bottom distributions of Chl and PM, it is hard to see any coherence beyond low values of both Chl and PM east of about 90°W and higher concentrations west of 90°W. Analysis and animations of water movement in this area by Zhang et al. (2012) show that surface water movement is complex and is influenced by changing winds, currents and inertial oscillations. Satellite images can provide some sense of synopticity in surface waters, but trying to obtain similar synopticity of bottom
conditions is impossible with only CTD stations. The Acrobat instrument provides an excellent opportunity to measure multiple parameters simultaneously and provide evidence of subpycnocline production and degradation and their relation to hypoxia.

**Acrobat Transects**

Selected Acrobat sections from Brown, Green and Blue waters will be discussed to identify important features that are evidence of subpycnocline production. This will be done using the background of the above results and discussion about PAR, nitrate, Chl, CDOM, and POC distributions. During June, unfavorable weather limited the number and length of Acrobat lines compared to August. The only line that can be compared well from both cruises is line 15. All other lines discussed in detail here will be from August. The beginning of each line is assumed to refer to the landward end of the line, even though the cruise track may have been run shoreward.

Acrobat line 16 (fig. 31) is 10 km northwest of, and parallels Southwest pass of the Mississippi Delta (fig. 3). Even this close to the river, the section doesn’t fully meet the Brown-water criterion of no surface production (no chlorophyll). PM ($b_b$), Chl, and CDOM were high in the surface 6-7 m of line 16, which, along with low salinity (<25), is consistent with these waters being part of the Mississippi River plume transitioning to highly productive surface waters. In surface waters concentrations of those three parameters decreased offshore. Below 7 m (subpycnocline), $O_2$ decreased and the mid water was hypoxic (<1.4 ml l$^{-1}$). Chl was near zero below the pycnocline, suggesting no primary production, while PM showed a low-concentration layer between 6-10 m, a
layer of increased concentration between 10-13 m, then decreasing concentration to ~3 mab where there was a thin nepheloid layer. This layering and bottom nepheloid layer suggest resuspension and advection of particles/sediment (Gardner, 1989). CDOM was high and stratified down to the pycnocline (7m) offshore with a 2-3 m thick band of CDOM matching the elevated PM layer and the hypoxic layer at 10-13 m, below which there was no CDOM. Mid-water hypoxic layers have been reported by Chen and Gardner (2004) and Chen et al., (2004) between 16 and 30m along isopycnal layers during cruises in the northern Gulf. These could possibly result from advection of detached nearby bottom boundary layers that contained terrestrial CDOM from surface to seafloor mixing in shallower water. The plot of b_b versus O_2 at different densities (fig. 24) shows coherence and mixing of these two properties along different density interfaces.

CTD profiles near the beginning (CTD L161) and 3 km beyond the seaward end of line 16 (CTD 162, fig. 26), showed that surface salinity increased from about 2 to 20 between those two sites (see fig. 3) indicating a declining influence of river plume water. The deeper water increased in salinity to >36 below 20 m out to a water depth of 45 m. Chl below the surface plume decreased to < 0.2 mg m^{-3} and PM also decreased to close to <0.5 mg l^{-1}, but then increased near the seafloor where salinity shows a drop of 4 in the bottom 2 m. A weak benthic nepheloid layer was present along all of line 16 (fig. 31) as evidenced by increased PM concentration.

Line 15 (August; fig. 32) crossed the inner shelf south of Barataria Bay (fig. 1). Surface salinity here was 26 at CTD L151 and decreased slightly to 24 at CTD L152,
seaward of line 15 (figs. 3). Bottom salinities at those two CTD stations were about 35 and 36 respectively, suggesting little mixing with river water. Both PM and fluorescence were elevated above the pycnocline, in the upper 10 m of the water column, but the concentrations decreased markedly south of 29.05°N for PM and south of 29.0°N for Chl. An anticyclonic gyre is often found outside of Barataria Bay (Ichiye, 1960; Wiseman et al., 1976), west of which the water typically moves westward along the shelf in non summer months (Cochrane and Kelly, 1986). CDOM was high (7-10 mg/m³) in the upper 10 m along the entire offshore transect. The lack of surface PM in the southern part of the transect suggests the possibility that both riverine and new marine-produced biogenic particles had been scavenged or settled, but the river plume was spreading both south and west, as traced by high CDOM and low salinity.

A 3-5 m area of hypoxic water was present at the seafloor on the inshore end of line 15 (August) with a corresponding area of increased CDOM and a smaller area of ~2 mg m⁻³ Chl. The high Chl area was localized, while the hypoxic water extended along the seafloor and also appeared to bifurcate with some hypoxic water being detached from the bottom and moving laterally, presumably along isopycnals. Values of PM reached as much as 8 mg l⁻¹ in the bottom boundary layer. That might be sufficient (depending on local density gradients) to increase the density of the water and exceed the vertical density stratification, so fresh sediments and organic matter settling from the plume (and possibly from resuspension) may be carried slowly across the shelf, providing organic matter for microbial respiration and oxygen consumption. Once such layers reach water of equal density, they can spread out along isopycnals (Cacchione and
Southard, 1974; Cacchione and Drake, 1986; McGrail and Carnes, 1983; Gardner, 1989).

Conditions along line 15 in June (fig. 33) were quite different from August (fig. 32). A surface lens of water low in salinity and high in CDOM, oxygen, PM and Chl thinned from 4 m to 0 m from the beginning of the transect. The main pycnocline was at about 10 m in both months. These distributions are consistent with a greater fresh-water discharge in June that was still carrying terrigenous particles, but with concentrations low enough that light was sufficient in the upper few meters to allow primary production of chlorophyll-containing organic matter that could settle to the seafloor. Bottom water along the transect had lower oxygen in June than August and there appeared to be intrusive layers of low-oxygen, high-CDOM water, presumably moving along density surfaces. These conditions are consistent with respiration of organic matter creating hypoxic to anoxic conditions and decay of phytoplankton creating marine CDOM on the seafloor and in intermediate layers, similar to those seen in this area by Chen et al., (2004). There was a small increase (1-2 mg l\(^{-1}\)) in Chl along the bottom, but this is more likely to be settled and resuspended Chl than in situ production.

Along line 13 (fig. 34) south of Terrebone Bay, the surface water plume varied from 4-7 m thick with a salinity less than ~25 and the pycnocline was at ~10 m. The water column was highly stratified with bottom salinities of about 35. Surface Chl and PM were high along the fresh-water plume and the mid water again showed extremely low concentrations of Chl and PM. Along the beginning of the transect Chl and PM were both high in the bottom 2-3 m. The same region had elevated CDOM. Chen et al.,
(2004) found that subpycnocline Chl and CDOM could result from subpycnocline production and decay of phytoplankton, but the CTD/PAR profile at the beginning of the transect (CTD cast L131 - fig. 35) showed that PAR is $< 1 \mu$mole photons m$^{-2}$ s$^{-1}$ at 8 m. This depth is the top of the Chl increase, so light was insufficient for subpycnocline production at that time. The bottom three meters of the CTD profile showed nearly uniform concentrations of all parameters, evidence of a bottom layer mixed by bottom shear (currents, tides) that keeps particles in suspension. The sediment trap data (Redalje et al., 1994; Zhang, 1997) indicate that in this area, enough carbon settles in about 20 days to utilize all O$_2$ in the bottom waters through respiration, plus there was abundant DOC for oxygen utilization. There is also a slight increase in CDOM in the bottom waters where PM and Chl are increased. These observations suggest that in this area the POC and Chl could have originated from one or both of two processes: 1) Chl-containing organic matter produced in surface waters could have settled and respired O$_2$ and produced CDOM on the seafloor or in the bottom mixed layer, or 2) there were times where light penetrated to the seafloor, contributing to primary production of Chl and organic matter, with subsequent degradation of some of that organic matter, producing CDOM.

The line south of Atchafalaya Bay (Line 10, fig. 36) started in Green waters and transitioned to Blue waters at about 22.88 °N and included areas that may have had subpycnocline production. The main pycnocline was at around 7 m for the first half of the transect. Chl was 1-2 mg m$^{-3}$ in surface waters at the start of the transect, increased below the pycnocline to a maximum of 5.5 mg m$^{-3}$ between 7-12 m for the first half of
the transect, but decreased to 1 mg m\(^{-3}\) near the bottom in the middle of the transect. The PM distribution did not match the Chl pattern well in this region. The highest Chl region had low PM, but there was extremely high PM at the bottom, deeper than the high Chl region, suggesting resuspended sediment. Resuspended sediment inhibits light and decreases primary production that would increase Chl. The second half of the transect had low PM (<0.5 mg l\(^{-1}\)) down to 10-15 m, below which both PM and Chl increased. Chen et al., (2004) have argued that subpycnocline production produces high-Chl subpycnocline waters, but in this region of the transect there was no matching increase in CDOM, which they said was evidence of phytoplankton degradation. Either there had not been time for degradation or the Chl source was different here from other areas where CDOM was found matching the Chl distribution. The only hypoxic area was at the start of the line where mid-water Chl was maximal. While this should be an area where oxygen is produced, it may be that the rate of utilization exceeds oxygen production.

West of Atchafalaya Bay, line 8 (fig. 37) was in typical Blue water with low PM and Chl (<1 mg m\(^{-3}\)) in surface water except near shore where all parameters were well-mixed to ~10 m, seen most clearly in PM. Chl, PM, CDOM, and salinity had increased concentrations in the bottom 1-4 m along the middle of the transect, and O\(_2\) was near or below hypoxic concentrations. While nutrient samples were not collected along the transect, station L081 at the beginning of the transect had 0.28 µM bottom nitrate, and station L082 at the end of the line had bottom nitrate of 2.58 µM (0.58 µM at the surface), so nitrate was available for production at the end of the transect. The higher
bottom nitrate might have come with the cool, saline water (T<25°C, S>36) that might have been brought in by the upwelling-favorable winds during August. As for light, these CTD stations were taken before 8 AM, so PAR measurements did not represent daylight conditions. The low O₂ near the seafloor suggests that degradation of available organic material was consuming oxygen faster than plankton could produce it. Sources of organic matter and the balance between production and consumption need further study for verification.

Transects west of 92.5°W mostly showed less stratification, moderate Chl and PM concentrations on the landward end of the transect, decreasing seaward. Transects also had high Chl in the bottom 1-2 m, elevated CDOM and a decrease in oxygen, though not < 1.4 ml l⁻¹, and therefore, not hypoxic.
CONCLUSIONS

The results of the June and August 2011 cruises along the Texas-Louisiana Shelf identified three types of areas in which different processes dominate as suggested by Rowe and Chapman (2002). Brown waters comprised the river outflow and initial plume where terrigenous particle concentration was large enough that it minimized primary production due to light limitation in surface waters. Green waters included the areas where particles had settled out sufficiently to allow substantial production in surface waters with abundant river nutrients, though nutrients decreased rapidly with distance from the river during June and August. Blue waters were identified as areas where nutrients had been depleted and particles had settled out or been consumed by zooplankton and settled from surface waters. Plume water could be traced from salinity and CDOM concentrations from fresh-water rivers to waters with salinity above 30 westward and offshore.

From results of this study, and from Chen et al., (2004) and Chen and Gardner (2004), a process that should be added to the Brown-Green-Blue concept of Rowe and Chapman (2002) is that occasionally beneath Green waters and frequently beneath Blue waters of the northern Gulf of Mexico, subpycnocline primary production occurs that generates oxygen and organic matter. Evidence for production is the presence of subpycnocline chlorophyll in areas where there is no surface chlorophyll that could act as a source of the bottom chlorophyll. Evidence for degradation is the distribution of marine CDOM in high-salinity bottom waters that matches subpycnocline chlorophyll
distributions. The deep marine CDOM is not connected with the surface terrestrial river CDOM.

Schaeffer et al., (2011) showed from satellite and in situ measurements that sufficient light for primary production reaches the seafloor and subpycnocline waters, producing oxygen and organic matter. Our light measurements confirmed that light frequently penetrates below the pycnocline, often reaching the seafloor in some areas. Nutrient concentrations (nitrate, nitrite, and ammonia) were rarely below accepted limiting levels during our field studies. The DOC in the water may be respired continuously and use enough oxygen to make the water nearly hypoxic. However, subpycnocline production can produce phytoplankton that yield more oxygen and prevent the water from becoming hypoxic. If production ceases because of light limitation (from an increase in phytoplankton abundance, sediment resuspension, or extended cloud cover), or nutrient limitation, the production-respiration balance may shift to net respiration. One would expect that fresh phytoplankton could be respired more quickly than older DOC based on work by Bianchi et al., (2002).

The effects of particle concentration and composition on potential hypoxic areas makes it particularly important to understand the role of PM and POC on the Texas-Louisiana Shelf. Bulk compositional analysis of filtered water samples and optical proxies showed higher concentrations and percentages of POC in June than August. Higher C:N ratios in August that June indicated a more degraded state of carbon in August. Based on carbon respiration rates, the standing stock of POC in June is sufficient to utilize enough oxygen to turn bottom waters containing 4 ml l\(^{-1}\) of oxygen to
hypoxic values (1.4 ml l\(^{-1}\)) in about 14 days. In August, the standing stock of POC in bottom waters would be utilized in 7 days and would use only half the amount of oxygen necessary to turn bottom waters hypoxic. Calculations from sediment trap carbon flux measurements in this area in previous years combined with our measurements of POC standing stock in bottom waters indicate that the average POC standing stock of mid and bottom waters during the our field studies can be replenished about every 10 days in the summer.

Regarding the direct relationship between particles and hypoxia, there is no simple, consistent correlation – it is a complex balance that includes conservative and non-conservative components and processes that are all time-varying, sometimes rapidly. Inorganic particles (sediment and phytoplankton skeletons) influence hypoxia only by potentially shading light and limiting primary production. Bottom sediment can be resuspended and decrease light penetration. Resuspension can also carry organic matter into the bottom mixed layer for oxygen utilization with possible lateral advection from sloping boundaries along isopycnals. Organic particles can shade light from underlying waters but are also a source for oxygen utilization through respiration by microbial processes. Phytoplankton can produce oxygen – even in subpycnocline, hypoxic waters if nutrients are present. The organic carbon that subpycnocline plankton produce eventually becomes available for oxygen consumption when plankton die or are consumed. Benthic production and respiration cannot produce a net reduction of O\(_2\), but the respiration rate of fresh phytoplankton might be faster than respiration of refractory
components of DOC, influencing the timing of hypoxic events - a hypothesis that needs further investigation.

The high temporal and spatial resolution made possible with new instruments aids in unraveling mechanisms of hypoxia by making simultaneous measurements of multiple relevant parameters. Further studies should be made to understand time scales and processes that control oxygen concentrations in the northern Gulf of Mexico, including measurements of primary production in subpynocline waters, and time series measurements of light, nutrients, chlorophyll, turbidity, oxygen, wind, currents and settling carbon fluxes to aid in modeling these complex processes.
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Figure 1. Frequency of hypoxia from 1985 to 2008 (Rabalais et al., 2007; SAB, 2007).
Figure 2. Processes forming hypoxia in different zones or water types in the northern Gulf of Mexico as proposed by Rowe and Chapman (2002).
Figure 3. CTD stations (dots), Acrobat transects (red lines), along-shelf transect (blue line), for (A) June and (B) August, 2011.
Figure 4. Mississippi River flow at Baton Rouge, LA, for 2007-2013. Yellow curve is the 7-year median daily value and blue is the daily discharge. Data from USGS (http://nwis.waterdata.usgs.gov).
Figure 5. Maps of chlorophyll $a$ from MODIS ocean color data with station locations during (A) June 26-July 3 and (B) August 5-12, 2011. Note logarithmic scale.
Figure 6. Eleven-year average (1997-2007) of % PAR reaching the seafloor as calculated by Schaeffer et al. (2011) for (A) June and (B) August. Dots indicate our CTD stations in 2011 (note that scales are not linear).
Figure 7. Laboratory calibrations of (A) PM (using surface sediment <8µm) vs. b₀ for both the CTD (open triangles) and Acrobat (solid triangles) FLNTU instruments, and (B) b₀ of the Acrobat FLNTU (967) vs. CTD FLNTU (2276).
Figure 8. Bottom sample PM concentrations vs. $b_b$ for (A) June and (B) August.

For June:
- Equation: $y = 1.099x - 5.173$
- $R^2 = 0.875$
- $P < 0.001$

For August:
- Equation: $y = 1.236x - 5.347$
- $R^2 = 0.911$
- $P < 0.001$
Figure 9. POC concentrations vs. $b_b$ for June in (A) surface, (B) middle, and (C) bottom waters.
Figure 10. POC concentrations vs. $b_b$ for August in (A) surface, (B) middle, (C) and bottom waters.
Figure 11. Combined middle- and bottom-water PM concentrations vs. $b_b$ for (A) June and (B) August.

\[ y = 0.992x - 4.105 \]
\[ R^2 = 0.888 \]
\[ P < 0.001 \]

\[ y = 1.185x - 4.787 \]
\[ R^2 = 0.917 \]
\[ P < 0.001 \]
Figure 12. Shipboard flowthrough PM concentrations vs. \( c_p \) for (A) June combined, and POC concentrations vs. \( c_p \) for (B) June and (C) August.
Figure 13. Along-shelf transect (~20 m contour, blue line in figure 3) of surface temperature, salinity, c_p (PM), and CDOM for June.
Figure 14. Along shelf transect (~20 m contour, blue line in figure 3) of surface temperature, salinity, $c_p$ (PM), and CDOM for August.
Figure 15. Correlation between salinity and CDOM for the along-shelf transect (blue line in figure 3A and B) in June (black) and August (red).
Figure 16. Surface CDOM along the cruise track in (A) June and (B) August.
Figure 17. Surface PM concentrations as calculated from $c_p$ along the cruise track in (A) June and (B) August. Black indicates > 14 mg l$^{-1}$. 
Figure 18. Bottom PM concentrations as calculated from $b_b$ (see fig. 8) in (A) June and (B) August.
Figure 19. Bottom POC concentrations as calculated from $b_b$ (see figs. 9 and 10) in (A) June and (B) August.
Figure 20. POC concentrations (mg l\(^{-1}\)) by longitude in middle and bottom waters for June and August. Solid symbols were from hypoxic waters.
Figure 21. Percent POC concentrations by longitude in (A) surface, (B) middle, and (C) bottom waters.
Figure 22. C:N ratios by longitude in (A) surface, (B) middle, and (C) bottom waters.
Figure 23. Oxygen content in bottom waters as mapped by S.F. DiMarco (personal communication) using CTD profiles and Acrobat transects for (A) June and (B) August, 2011.
Figure 24. Graph of $b_b$ (proxy for PM) versus $O_2$ for all data along Acrobat Line 16 (see fig. 3 for location). Data are colored based on density levels ($\sigma_T$). See text for discussion.
Figure 25. True color MODIS image of the Texas-Louisiana shelf on October 11, 2008 (NASA Earth Data, http://rapidfire.sci.gsfc.nasa.gov/gallery).
Figure 26. CTD profiles of Chl fluorescence, PM (b\textsubscript{b}), Oxygen, Salinity, Temperature, and PAR at stations within (A) Brown-Sta L162, (B) Green- Sta L142, and (C) Blue- Sta L082 waters (See fig. 3 for locations).
Figure 27. Satellite map of the depth (m) at which PAR is 1% of surface PAR averaged over an eight day period for (A) June 26-July 3 and (B) August 5-12, 2011 with our CTD station locations (note that scales are not linear).
Figure 28. Nitrate concentrations (µM) in surface waters for (A) June and (B) August, and in bottom waters for (C) June and (D) August. Triangles mark stations with nitrate concentrations < 0.5µM.
Figure 29. DIN concentrations (=NO₃ + NO₂ + NH₄) in surface waters for (A) June and (B) August, and in bottom waters for (C) June and (D) August. Triangles mark stations with DIN concentrations < 1 µM.
Figure 30. Chl concentrations (mg m$^{-3}$) in surface waters for (A) June and (B) August and in bottom waters for (C) June and (D) August.
Figure 31. Acrobat Line 16 in August: (A) Density ($\sigma_T$), (B) salinity, (C) CDOM, (D) oxygen, (E) PM, and (F) Chl. Black indicates parameter $>$ scale maximum. Note different latitude scale from other Acrobat Lines.
Figure 32. Acrobat Line 15 in August: (A) Density ($\sigma_T$), (B) salinity, (C) CDOM, (D) oxygen, (E) PM, and (F) Chl.
Figure 33. Acrobat Line 15 in June: (A) Density ($\sigma_T$), (B) salinity, (C) CDOM, (D) oxygen, (E) PM, and (F) Chl. Note different latitude scale from figure 32.
Figure 34. Acrobat Line 13 in August: (A) Density ($\sigma_T$), (B) salinity, (C) CDOM, (D) oxygen, (E) PM, and (F) Chl.
Figure 35. CTD profile at station L131 in August (see fig. 3b): Chl fluorescence, PM ($b_b$), Oxygen, Salinity, Temperature, and PAR.
Figure 36. Acrobat Line 10 in August: (A) Density ($\sigma_T$), (B) salinity, (C) CDOM, (D) oxygen, (E) PM, and (F) Chl.
Figure 37. Acrobat Line 8 in August: (A) Density ($\sigma_T$), (B) salinity, (C) CDOM, (D) oxygen, (E) PM, and (F) Chl.