INFLUENCES ON THE TEMPORAL AND SPATIAL VARIABILITY OF

PARTICULATE MATTER IN THE NORTHERN GULF OF MEXICO

A Thesis

by

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ABSTRACT

The Mississippi River drains more than 3 million km^2 of the North American continent and discharges 240 million metric tons of sediment and 1.35 million metric tons of nutrients annually into the Gulf of Mexico. This increase occurs primarily in the late winter and early spring, with nutrients fueling large algal blooms. The organic matter produced is grazed by zooplankton and decays as it sinks. The decaying organic matter utilizes oxygen, resulting in hypoxic conditions below the pycnocline when oxygen cannot be replenished by mixing. Measurements of oceanographic properties, including dissolved oxygen, temperature, salinity, and particle backscatter, were made with sensors on the CTD casts in June and August of 2010-2014 on the Texas-Louisiana shelf from Galveston Bay to the Mississippi River. These discharge conditions of these cruises are designed as flood, normal or drought based on the USGS Drought monitoring criteria. Discrete samples were collected from bottles on the CTD rosette, and continuous measurements were made with a towed undulating vehicle and a shipboard flow-through system.

Particulate matter (PM) concentrations in the surface waters increased with greater river discharge only during one flood period compared to a drought and normal period, showed no difference in concentration in months closer to peak discharge (June) compared with later (August) except in 2013, and showed increases in PM concentration for surface waters in areas closer to the freshwater sources (Mississippi, Atchafalaya, and Terrebonne Bay). Bottom PM concentrations increased with an increase in river

discharge during a flood event when compared to a drought or normal event, indicated no difference in concentration in June (closer to peak discharge) compared with August, except again in 2013, and did not show a decrease with distance from the riverine source. Particulate organic carbon (POC) concentrations in the surface waters increase with increased river discharge during flood conditions, in months closer to peak discharge (June) compared with later (August), and in areas closer to river input. POC concentrations in the bottom waters do not show a difference with increase in river discharge or during months closer to peak discharge (June) compared with later (August) in any areas.

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1. INTRODUCTION

1.1 Background

1.1.1 Background of the Mississippi River system

The Mississippi River system drains more than 3 million km^2, roughly 40%, of North America, and is the sixth largest freshwater discharge system in the world (Milliman and Meade, 1983). The Mississippi River system discharges over 240 million metric tons of sediments and 1.35 million metric tons of nutrients annually into the Gulf of Mexico (Coleman and Wright, 1975), and is the main outlet for agricultural and industrial runoff as well as the main outlet for solutes, sediment, and freshwater to the Gulf of Mexico (Turner and Rabalais, 1991; Blum and Roberts, 2012). The freshwater discharge into the Gulf of Mexico has a maximum volume during the spring, due to melting snow and increased rainfall in the Mississippi drainage basin (Wiseman, et al., 1997; Rabalais, et al., 2002b; Allison, et al., 2013). Prior to 1963, the Atchafalaya River started to capture more water than the Mississippi River, indicating a natural, gradual shift of the flow volume. In 1963, near Simmesport, Louisiana, 215 km upstream from the Mississippi River mouth, the Army Corps of Engineers built the Old River Flood Control structure on the Mississippi River to control the amount of water that flows to the Lower Mississippi River, 70%, and to the Atchafalaya River, 30% (Neill and Allison, 2005; Xu et al., 2011).

The Balize Delta, or Birdsfoot Delta, is one of the two most recent delta complexes that the Mississippi River has created (Coleman, et al., 1998; Blum and

Roberts, 2012). The large amount of sediment that is released through the Balize Delta, approximately 160 million metric tons annually, has created an area of rapid deposition and rapid delta progradation onto a narrow and steep continental shelf (Allison, et al., 2000). The sediment from the river discharge travels approximately 30 km or less both to the east and the west of the river mouth and some sediment can be deposited in waters deeper than 100 m up to 40 km to the south (Corbett, et al., 2004; Xu, et al., 2011).

The Atchafalaya River is an early stage distributary of the Mississippi River and the mouth is located 210 km west of the Mississippi River mouth (Allison, et al., 2000; Neill and Allison, 2005). The river discharges into the Atchafalaya Bay at both the river mouth and the artificial Wax Lake outlet (Neill and Allison, 2005). The Atchafalaya Bay is shallow and broad with a gentle slope (Neill and Allison, 2005). The Atchafalaya releases a smaller amount of sediment than the Mississippi, approximately 80 million metric tons annually. The bay is shallow, with an average depth of 2-3 meters, so storms resuspended sediment that can in turn be advected out of the bay (Allison, et al., 2000). As a result of resuspension and advection, only 27% of the sediment is deposited in the bay (Neill and Allison, 2005; Bianchi, et al., 2010; Xu et al., 2011). The sediment that is not trapped in the bay is deposited on the northern Gulf of Mexico inner continental shelf, in waters up to 50 m deep (Bianchi, et al., 2010; Xu, et al., 2011).

1.1.2 Description of hypoxia

Coastal hypoxia, or the depletion of oxygen, is increasing as anthropogenic eutrophication increases (Diaz and Rosenberg, 1995; Rabalais, et al., 2009). In the northern Gulf of Mexico, a seasonal hypoxic zone has been observed directly since at least the early 1970s (Rabalais, et al., 2002a); however, hypoxia in the northern Gulf of Mexico has been occurring since the late 1800s, based on foraminifera proxy for hypoxia (Osterman, et al., 2005). The Gulf of Mexico hypoxic area is the second largest hypoxic area in the world and the largest hypoxic zone in the western hemisphere (Rabalais et al., 2002a). Hypoxia in the northern Gulf of Mexico is defined as waters with dissolved oxygen concentrations of 1.4ml/L or lower (Rabalais et al., 2002b; Diaz and Rosenberg, 2011). Below this dissolved oxygen concentration, shrimp and demersal fish are not caught with bottom trawls, and presumably die or leave the area to find waters with higher oxygen content (Rabalais et al., 2002a; Diaz and Rosenberg, 2011). The hypoxic zone in the Gulf of Mexico is observed on the continental shelf west of the Mississippi River, and follows a seasonal cycle, increasing substantially during June-August, and dissipating in the winter (Wiseman, et al., 1997; Rabalais, et al., 2002a; Hetland and DiMarco, 2008).

An increase in nutrients and stratification from spring through summer influence the formation of hypoxia in the Gulf of Mexico. As nutrient-laden river water, from wastewater and fertilizer runoff, reaches the Gulf of Mexico, and daylight hours increase, phytoplankton blooms are generated (Rabalais et al., 2002a). Zooplankton fecal pellets and plankton that are not consumed sink through the water column (Rabalais et al., 2002b; Rowe and Chapman, 2002). This organic material undergoes respiration in the water column and on the seafloor, which consumes oxygen, and if oxygen cannot be replenished, the waters may become hypoxic (Rabalais et al., 2002a; Hopkinson and Smith, 2005; Rowe and Deming, 2011). Persistence of a strong pycnocline decreases wind-driven mixing. As the Mississippi River discharges freshwater into the Gulf of Mexico, the fresher, less dense water remains atop the denser, saltier water of the Gulf, creating a sharp pycnocline (Rabalais, et al., 2002a; Hetland and DiMarco, 2008). Strong easterly winds during all but the summer months create downwelling favorable conditions (Cochrane and Kelly, 1986). The westerly winds during summer are weaker, so less water column mixing occurs and dissolved oxygen is not replenished in sub-pycnocline waters by mixing. Upwelling is favored during the summer, increasing the movement of the freshwater plumes from the rivers to offshore. The westerly winds weaken enough to increase the stratification of the Mississippi River plume over a wider area and enhance hypoxia (Cochrane and Kelly, 1986; Wiseman, et al., 1997; Hetland and DiMarco, 2008; Son, et al., 2012). Bacterial decomposition of the organic matter below the pycnocline utilizes oxygen, which contributes to hypoxic conditions (Hetland and DiMarco, 2008; Bianchi, et al., 2010).

Most sediment carried by the river flocculates when mixed with salt water, so areas further from the river source have clearer waters. If sunlight can penetrate below the pycnocline, sub-pycnocline primary production can occur, resulting in bottom waters remaining oxygenated or becoming re-oxygenated (Lehrter, et al., 2009). During a series of seven cruises from 2005-2007, 25-50% of the primary production observed on the Texas- Louisiana shelf was due to the sub-pycnocline production (Lehrter, et al., 2009). The sub-pycnocline production, while not very abundant at times, is also responsible for providing just enough dissolved oxygen that the waters off the coast of Louisiana stay hypoxic and do not become anoxic (Lehrter, et al., 2009). However, during years of high river discharge, or floods periods, a larger amount of particulate matter enters the Gulf of Mexico, decreasing the amount of light that can penetrate throughout the water column (Lehrter, et al., 2009; Cai, et al, 2015). The light limitation due to particulate matter in the water column is observed to be strongest near the Mississippi River and weakest further away from the Mississippi River input (Lehrter, et al., 2009; Xu, et al., 2011). These areas of light limitation also coincide with areas of observed hypoxia (Schaeffer, et al., 2011). In shallow water, i.e., water depths less than ~ 10 meters, depending on wave heights, sediment can be resuspended throughout the water column due to localized wind and wave mixing. Strong currents and strong storms can resuspend sediment from deeper depths, re-introducing particulate matter with about 1-3% organic carbon back into the overlying water (Zhang, 1997). This input can stimulate microbial remineralization of organic matter in the bottom of the water column, therefore enhancing both the extent and severity of hypoxia (Wainright and Hopkinson, 1997; Bianchi, et al., 2010; Xu, et al., 2011). Locations where this influence of sediment has the greatest potential to fuel hypoxia are in bottom waters on the inner and middle continental shelf near the Mississippi and Atchafalaya River mouths (Lehrter, et al., 2009).

Usually in September, the discharge of the Mississippi and Atchafalaya Rivers reaches its minimum discharge and westerly winds begin to strengthen, reducing stratification and nutrient supplies and decreasing phytoplankton production (Bianchi, et al., 2010; DiMarco, et al., 2010). The autumn is also the onset of stronger easterly winds, northerly winter storms, and colder temperatures in the Gulf of Mexico; the wind, waves and colder air help to break down the stratification in the water column and the bottom waters become re-oxygenated (Wiseman, et al., 1997; Neill and Allison, 2005; DiMarco, et al., 2010).

Hypoxia is harmful to the ecosystem. The diversity in hypoxic ecosystems decreases as organisms move away from the hypoxic areas or die due to the lack of oxygen which results in a decrease in the complexity of the food web (Harper, et al., 1981; Rabalais, et al., 2002a). The fauna in the area decreases and may not recover if the hypoxic waters remain (Diaz and Rosenberg, 1995). Furthermore, hypoxia in the Gulf of Mexico has economic impacts. Off the Texas coast over the period of 1950-2000, an estimated 383 million, or about 30%, fish died due to environmental issues, including hypoxia, responsible for most of the fish kills, harmful algal blooms, and eutrophication (Thronson and Quigg, 2008). With the decrease in diversity and quantity of fish, the fishermen must fish for longer periods of time to catch the same amount of fish (Bianchi, et al., 2010; Diaz and Rosenberg, 2011). Furthermore, hypoxia causes economic impacts; the Louisiana-Texas continental shelf provides 30% of the coastal commercial fisheries in the United States and provides almost $1 billion in seafood annually (Xu, et al., 2011; Blum and Roberts, 2012). As hypoxia increases, the financial contribution to the Louisiana economy decreases. Additionally, the amount of seafood available for human consumption also decreases due to hypoxia (Rabalais, et al., 2002b; Bianchi, et al., 2010; Blum and Roberts, 2012).

1.1.3 Locations of hypoxia in the Gulf of Mexico

The hypoxic zone in the Gulf of Mexico usually occurs in water depths of 5-30 m and is found in 20-50% of the water column at any given location, but can include up to 80% of the water column in shallower areas. Hypoxia can be found in depths up to of 60 m and in areas as close to shore as 1 km and as far offshore as 125 km, extending from the Louisiana shelf to the Texas shelf (Rabalais, et al., 2002b). The average area of the hypoxic zone is about 16,600 km^2 for years 2007-2011 (Obenour, et al., 2013); with the largest area in 2007 at 20,500 km^2 (DiMarco, et al., 2010).

Based on model outputs, regions to the east of 90.5 ^{o} W are affected primarily by the Mississippi River input (Hetland and DiMarco, 2008). The Mississippi River brings an increase of nutrients to the Gulf of Mexico, and plankton blooms increase the amount of dissolved oxygen in surface waters. However, as remineralization of the detritus occurs in the water column, the dissolved oxygen is consumed creating hypoxic bottom waters below the pycnocline (Bianchi, et al., 2010). Based on the models, the region to the west of 90.5^{o}W is primarily affected by the Atchafalaya River (Hetland and DiMarco, 2008). West of Terrebonne Bay and south of the Atchafalaya Bay, hypoxia is controlled more by benthic respiration than water-column respiration (Hetland and DiMarco, 2008; Bianchi, et al., 2010). Hypoxia in offshore areas is due to fallout of organic matter from phytoplankton blooms south of Terrebonne Bay at 90.3^o W (Rowe and Chapman, 2002), and between Barataria Bay and Timbalier Bay (Rabalais, et al., 2002a).

Four zones have been identified to classify the mechanisms that control hypoxia under different conditions in the northern Gulf of Mexico, shown in Figure 1 (Dale, et al., 2010). Zone 1 is located closest to the mouths of both the Atchafalaya and Mississippi Rivers. This zone is characterized by strong water column stratification and respiration of large amounts of organic carbon from nutrient-stimulated primary production in the surface waters and riverine input (Dale, et al., 2010). Due to the large amount of organic and inorganic material in the water, light is limited in the lower water column and primary production is limited to surface waters in this region (Bianchi, et al., 2010; Dale, et al., 2010). Hypoxia in this area is controlled by water column respiration from eutrophication (Dale, et al., 2010).

Zone 4 is immediately offshore of Zone 1 and parallels the coast. Zone 4 exhibits high primary production due to the coastal boundary layer, or the nearshore zone of vertically well-mixed water. Mixing within this layer can enrich the surface waters with fresh nutrients, increasing primary production in surface waters, which can deliver more organic detritus to bottom waters. As the organic detritus is moved out of Zone 2 to Zone 4, hypoxia in the bottom waters can increase due to respiration of the organic material (Boesch, 2003).

Zone 2 is an intermediate area located further off shelf from the river source and is similar in characteristics to the "Green Zone" described in Rowe and Chapman (2002). Zone 2 is the location of highest surface primary production. Here, most of the sediment has settled out of the water column, allowing for more light penetration, and water column stratification is still strong. Nutrients from the river are still abundant, creating large phytoplankton blooms. In this zone, hypoxia is fueled by nutrient-stimulated production in surface waters and water column respiration (Rowe and Chapman, 2002; Dale, et al, 2010).

Zone 3 is located the furthest from both river sources. Here, nutrients in the surface waters are limited, but organic matter from Zones 2 and 4 can be deposited on the bottom of Zone 3. Microbial respiration in sediments controls most of the formation of hypoxia in this area (Dale, et al., 2010).

1.1.4 Hypoxia during flood and drought years

During years of increased discharge, more freshwater, sediment, and nutrients are transported into the Gulf of Mexico. As the nutrient load and stratification increase, phytoplankton blooms also increase, resulting in a larger and more widespread area of hypoxia. Abnormally high discharge occurred in 1993, and created widespread areas of low salinity waters as well as a significantly larger hypoxic zone than in previous years (Wiseman, et al., 1997; Xu, et al., 2011). Floods increase the amount of nutrients, thus producing more organic matter than can be remineralized in the water column, enhancing a strong hypoxic event. Therefore, the sediment accumulating on the seafloor may store an above-average amount of organic matter that remains through a mild winter. If those sediments are resuspended the following year, the organic matter can re-enter the bottom waters that were re-oxygenated during the winter, allowing bacteria to remineralize the organic material and in the process, again depleting the waters of oxygen (Wiseman, et al., 1997; Rowe and Chapman, 2002; Xu, et al., 2011). Conversely, drought conditions have below average discharge and nutrient input.

During these years, hypoxia is not as widespread or severe, and the re-oxygenation of waters occurs earlier and more rapidly, due to the decline in river input (Wiseman, et al., 1997).

1.2 Objectives and Hypotheses

The main objective of this work is to analyze temporal and spatial variations in particulate matter (PM), particulate organic carbon (POC), and carbon to nitrogen (C:N) ratios in the Gulf of Mexico in the context of varying discharge of the Atchafalaya-Mississippi River system. Data collected on research cruises during June and August in the summers of 2011, 2012, 2013, and 2014 will be compared to test the following hypotheses:

I. PM and POC concentrations and C:N ratios in the surface and bottom waters are statistically different inter-annually with variations in river water discharge.

II. PM and POC concentrations and C:N ratios in the surface and bottom waters are statistically different between June and August of each year 2011-2013.

III. Increased river discharge supports an increase in concentrations of PM and POC at the surface near the freshwater source, but not in the outer regions of the shelf.

IV. Changes in river discharge have little impact on concentrations of PM in bottom waters, either near the river source or in regions away from the river source.

To test hypotheses 1 and 2, bottle sample concentrations will be compared based on the classification of discharge; flood, normal flow, or drought, based on Figure 2 and listed in Table 1 for hypothesis 1, and bottle sample concentrations will be compared based on the month of collection, June or August, for each year for hypothesis 2. Because the data are not normally distributed, a Wilcoxon Rank Sum Test will be used to test the hypothesis. For hypothesis 1, the hypothesis holds true if either surface or bottom PM and POC concentrations or C:N ratios do differ between the flood, normal, and drought conditions. For hypothesis 2, the hypothesis holds true if either surface or bottom PM and POC concentrations or C:N ratios do differ between June and August.

To test hypothesis 3, five areas, referred to as boxes, in the northern Gulf of Mexico (Figure 3) will be analyzed based on data from Acrobat lines, shown in Figure 4a. Backscatter measured from the CTD casts will be used as a proxy for PM concentrations, based on Figure 5 and Table 4. POC concentrations are calculated from MODIS-Aqua 4km satellite data with the algorithm of Stramski, et al. (2008). Giovanni software was used to compile and plot monthly averages of POC concentrations. Monthly averages are based on 8-day composite images. Figure 6 shows boxed areas with Acrobat lines and Figure 7 shows the same boxes on a map of satellite-derived POC. A box near the Mississippi River (Mississippi Box) includes Acrobat lines L15 and L16, and will be compared with monthly mean discharge data for the Mississippi River. A box near the Atchafalaya Bay (Atchafalaya Box) includes Acrobat lines L08, L09, and L10, and will be compared with monthly mean discharge data for the Atchafalaya River. A small area near Terrebonne Bay (Terrebonne Box) is chosen based on the area of prevalent bottom hypoxia (Rabalais, et al., 2007) and includes Acrobat lines L12, L13, and L14, and will be compared with the combined monthly mean Mississippi and Atchafalaya River discharges. As the influence of small tributaries is very small compared to the combined discharge, they will not be considered. A small area south of Lake Sabine (Sabine Box) is included to examine the shelf in the western part of the study area and encompasses Acrobat line L06; the Sabine Box will be compared with the combined monthly mean Mississippi and Atchafalaya River discharges as they are three orders of magnitude higher than that of Sabine River. Additionally, an area on the central portion of the mid-shelf (Mid-Shelf Box) is included to examine satellite data for POC concentrations and will also be compared with combined monthly mean Mississippi and Atchafalaya River discharges. The Mid-Shelf Box is chosen to be on the shelf in waters of similar depth of the previously mentioned areas, but at a location south of the Atchafalaya Bay. A rectangle of the Northern Gulf of Mexico (NGOM Box) that includes all sampled areas is examined to compare POC concentrations averaged across the whole shelf with combined river discharge. The NGOM Box will not be used to compare PM concentrations as the NGOM Box covers a much greater area than all the Acrobat sections.

Areas that will be considered “near source” are the Mississippi Box, Terrebonne Box, and Atchafalaya Box. Areas that will be considered “far from source” are the Sabine Box and Mid-Shelf Box. POC concentrations and PM concentrations will be compared with monthly river discharge for the Mississippi River, Atchafalaya Rivers, and those rivers combined. For this study, a strong correlation will have R^2 values of

0.64-1.0, a moderately strong correlation will have a R^2 value of 0.36-0.64, a moderate correlation will have a R^2 value of 0.16-0.36, a mild correlation will have a R^2 value of 0.04-0.16, and a weak correlation will have an R^2 value of 0.04 or less (Brewer, 2003). Hypothesis 3 holds true if either the surface POC or PM concentrations near the sources vary positively with changing monthly river discharge. Additionally, the hypothesis holds true if either the POC or PM concentrations far from the source vary positively with changing monthly discharge.

To test hypothesis 4, the Sabine, Atchafalaya, Terrebonne, and Mississippi boxes from hypothesis 3 will be used. For this test, because there are no Acrobat data for the Mid-Shelf Box, the Sabine Box will be considered as the only area further away from the source. Backscatter measured from CTD casts in bottom waters will be used as a proxy for PM concentrations, based on Figure 5 and Table 4. These backscatter values will be used to determine if any of the four areas observed correlate to changes in river discharge. The hypothesis holds true if bottom backscatter values change with changes in river discharge.

2. METHODS

2.1 Sample Collection and Lab Analysis

The methods and protocols described here were used during all cruises (Table 1) on the R/V Manta, owned by Flower Garden Banks Foundation and operated by National Oceanic and Atmospheric Association Flower Garden National Marine Sanctuary. Continuous water column profiles were made using a CTD Rosette (sampling stations indicated on Figure 4b) with six attached 4 L Niskin bottles, an FLNTU (measures backscatter and Chl fluorescence), and a dissolved oxygen probe, as detailed in Table 2. Two bottles (# 1 and 2) were tripped at the bottom of the water column, approximately 1 meter above the sediment water interface. Two bottles (# 3 and 4) were tripped in the middle of the water column at a depth determined by measuring the full water column depth and dividing it by two for a particular station. The last two bottles (# 5 and 6) were tripped within 1 meter of the surface.

Particulate matter (PM) was collected using a Poretics membrane filter, 0.40 µm pore size, 47 mm in diameter. The filters were placed on an anti-static strip and then weighed and placed in labeled, air-tight petri dishes until used for filtration. Water was retrieved from Niskin bottles at three nominal depths: bottom of the water column, middle of the water column, and top of the water column. The water was collected in a 500 mL bottle and stored out of sunlight until filtered. Collected water was vacuum-filtered within 14 hours of collection through the PM filters and rinsed 5 times with RO water to remove any salt water from the filters. Once filtered, the membrane filters were dried in an oven on low heat for approximately 10 minutes, placed back into airtight petri dishes, and placed in storage. After the cruise, the PM filters were weighed to obtain a sediment weight and stored in the sealed petri dishes.

Particulate organic carbon (POC) samples were collected and analyzed using processes outlined in Joint Global Ocean Flux Study (JGOFS) procedures. POC was measured using glass fiber filters (GF/F), 25 mm in diameter. Prior to use, the filters were combusted in an oven at $600^{o}C$ for 3-5 hours. Once dried, the filters were placed in a sealed container until used. During the cruise, water was drawn from Niskin bottles at three nominal depths: bottom of the water column, middle of the water column, and top of the water column. The water was collected in a 1 L opaque bottle and stored in shade until filtered. Collected water was vacuum filtered within 14 hours of collection through the GF/F filters, and then placed in tin foil and frozen until returning to the lab. An error occurred on MS09 (June 2014), where samples were rinsed 5 times with RO water to remove any salt residue before being wrapped in tin foil and frozen. The POC and PON measurements for June 2014 will not be considered. Upon return, the POC filters were transferred from the tin foil into glass tubes. The tubes were dried at $38^{o}C$ for 5 hours. Once dried, the uncapped tubes with filters were placed in a desiccator containing hydrochloric acid and were fumigated for 20 hours to remove calcium carbonate. After fumigation, the filters were again dried at $38^{o}C$ for 5 hours. After being dried the second time, the POC filters were wrapped in 30mm tin disks and stored in a 96-well-plate sample holder. Samples were sent to the Virginia Institute of Marine Science for POC and PON measurements on an Eager CHN elemental analyzer. Samples on MS03 (June

2011) and MS04 (August 2011) were collected in the same manner and processed at Texas A&M University as described by Cochran (2013).

A Sea Sciences, Inc. undulating towed vehicle, the Acrobat, was used to collect continuous profiling data along cross-shelf sections in the Northern Gulf of Mexico. Instruments on the Acrobat measured pressure, salinity, temperature, dissolved oxygen, colored dissolved organic matter (CDOM) fluorescence, turbidity, and chlorophyll *a* fluorescence as shown in Table 2. The Acrobat was towed behind the ship along predetermined lines that were perpendicular to the coast to create vertical sections of the various properties. Each undulation of the Acrobat was from 1-2 meters below the surface to 1-2 meters above the seafloor and then back to the surface, and was completed about every 200 meters along each transect path (DiMarco, 2013). The planned Acrobat tow lines for all cruises are similar to those for cruise MS07 (June 2013) in Figure 4a.

3. RESULTS

PM, POC and C:N were determined from bottle samples taken during seven cruises over a four year period (2011 - 2014) which spanned varying discharge conditions (Table 1, Figure 2). The concentrations of PM and POC and the C:N ratios from the bottle samples were divided into three data sets of samples taken at the nominal top, middle, and bottom depths of the water column. Linear regressions of the concentrations of PM and POC with particle backscatter (b_b) obtained from the CTD FLNTU are used to create algorithms for estimating concentrations of PM and POC from the optical data. The comparisons for one cruise are shown in Figure 5, and results from the remaining cruises are listed in Table 4; there is a strong correlation between particle backscatter and PM (Figure 5) but not POC, so particle backscatter will only be used as a proxy for PM concentrations.

The seven cruises were separated into flood, normal, and drought river discharge conditions based on Figure 2 and listed in Table 1. Flood and drought conditions are based on the U.S. Drought Monitor system of classification. Using monthly mean discharge data from 2004-2014, any discharge above the 80^{th} percentile of the 10-year average is considered a flood condition. Conversely, any discharge below the 20^{th} percentile of the 10-year averages is considered a drought condition. Cruises that fall between the 20^{th} and 80^{th} percentile for the 10-year average are considered normal conditions. Based on the discharge for the Mississippi River at the Baton Rouge, LA station, the cruises that have discharge rates above the 80^{th} percentile are MS03 in June

2011 and MS07 in June 2013. Cruises that classify as drought conditions and have discharges below the 20th percentile are MS05 in June 2012 and MS06 in August 2012. Normal conditions cruses are MS04 in August 2011, MS08 in August 2013, and MS09 in June 2014.

Statistical comparisons of flood classifications and monthly comparisons were made using the Wilcoxon Rank Sum Test, an alternative to the two-sample t-test, which is used when data are not uniformly distributed, such as these highly skewed data. The test is based on the rank order of the samples, and it does not use the actual values of the samples. The P-values determine the probability that the null hypothesis is rejected. A 95% confidence level was used for all data sets. When the null hypothesis is rejected, the alternative hypothesis is confirmed and the data sets have a statistical difference at a confidence level of 1- p value. For Tables 5-8, “Reject” is referring to the null hypothesis, that there is no difference in the distributions, so all results that are rejected in the test do have a difference between the two cruises.

Six areas were outlined in the northern Gulf of Mexico as described in the Objectives and Hypotheses (Figure 4). Within the NGOM box that covers the entire study area, five sub areas were created: the Mississippi, Atchafalaya, and Terrebonne Boxes are areas near freshwater sources and the Sabine and Mid-Shelf Boxes are areas further from freshwater sources. The surface PM and satellite POC will be compared with river discharge for the Mississippi River, Atchafalaya River, or the combined rivers, as outlined in the Hypotheses and Objectives. For all boxes, relationships between mean river discharge and PM or POC concentrations are classified as weak, mild, moderate, moderately strong, or strong as outlined in the Objective and Hypotheses.

Average monthly surface POC concentrations were determined from MODIS-Aqua 4km satellite data for January 2011 through September 2014 using the algorithm of Stramski, et al. (2008) and Giovanni software. Average monthly discharge for the Baton Rouge station (USGS 07374000) on the Mississippi River is used for the Mississippi Box. The travel time of Mississippi River water in normal flow conditions from the Baton Rouge station to the Mississippi Delta, approximately 229 miles at 3 mph, is approximately 76 days ("Mississippi River Facts", 2016; "Mississippi Mile Markers and Speed", 2016). Average monthly discharge rates for the Simmesport, LA station (USGS 07381490) on the Atchafalaya River are used for the Atchafalaya Box. While there are various smaller rivers that discharge into the Gulf of Mexico, as well as distributaries off of the main rivers, only the average monthly discharge of Baton Rouge and Simmesport stations will be combined when making comparisons of mean PM or POC concentrations for the Sabine, Terrebonne, Mid-Shelf, and NGOM Boxes. The time series for the three river discharges are shown in Figure 8. Each box will have monthly mean surface POC concentrations, obtained from the MODIS-AQUA satellite data and the Stramski, et al. (2008) algorithm, and is compared with the associated river discharges as well as surface and bottom backscatter values compared with the associated river discharges, to determine if a statistically significant relationship, defined in Objectives and Hypotheses, exists. The northern Gulf of Mexico (NGOM) Box is used to determine if the monthly mean surface POC concentrations determined via satellite measurements varied with river discharge for this large-scale area (Figure 9). POC concentrations for June and August of 2011 and June 2014 and C:N ratios for 2014 are not compared as they were processed differently.

Surface and bottom PM concentrations are obtained from bottle samples as well as particle backscatter for surface and bottom values from the Acrobat transects. Acrobat data used for surface comparisons are 2-3 meters below the surface of the water for every undulation in order to avoid bubbles at the very surface. Acrobat data used for bottom comparisons are the bottom 1-2 meters of every undulation. Not all undulations reached the threshold for surface or bottom measurements. Additionally, the average backscatter values from each undulation for both the surface and bottom measurements are averaged along a transect to obtain a value for comparison. Mean surface backscatter along Acrobat lines in three boxes (Figure 6) are compared with river discharge. Backscatter (bb) has a linear correlation with PM concentration (Figure 5), so bb is used as a proxy for PM.

4. DISCUSSION

4.1. Hypothesis 1- PM and POC concentrations and C:N ratios in the surface and bottom waters are statistically different inter-annually with variations in river water discharge.

For surface and bottom bottle samples, PM and POC concentrations and C:N ratios were obtained over a series of CTD casts (Figure 4b) and the seven cruises were separated into flood, normal and drought river discharge classifications based on the US Drought Monitor System classification.

4.1.1 Inter-annual differences in PM concentrations with changing river discharge

During the flood conditions for June 2011, surface water PM concentrations are not statistically different (p-value >0.05) than drought conditions in June 2012 or normal conditions in June 2014 (Figure 10, Table 5). In June 2011, due to instrument malfunctions, fewer stations were sampled than in 2012, 2013 and 2014, including the stations that are shown to have higher values of PM concentrations such as in June 2013 ($89^{o} – 92^{o}$ West). This sampling bias could result in surface water PM concentrations for flood conditions in June 2011 cruise showing no difference between it and the drought conditions in June 2012 or normal conditions in June 2014. However, June 2011 and June 2013 do not show a statistical difference with a p-value of 0.0814. Surface water PM concentrations were statistically higher during flood conditions in June 2013 when compared to drought conditions in June 2012 (Figure 10) and statistically higher than normal conditions in June 2014 (Table 5). In addition to the measured increase of PM concentration in the surface waters in this study, other studies have shown increased concentrations of PM in the water column with increasing river discharge, in 1991 (Trefry, et al., 1994) and 2006-2008 (Cai, et al., 2015). The sources of surface water PM in the Gulf of Mexico are riverine input and primary production, so as river discharge increases, more PM in the surface waters is expected and observed. For the August months, the surface water PM concentrations for normal conditions in August of both 2011 and 2013 are not significantly different from drought conditions in August 2012 (Figure 11). This indicates that a large discharge increases the amount of PM in the surface waters in flood conditions, but there is a threshold of discharge that needs to be achieved in order to observe the increase in PM in the surface waters. The difference between drought conditions and normal conditions is not enough to reach that threshold for the August cruises, but is high enough for June cruises.

Bottom PM concentrations for June cruises are also not statistically different for the flood conditions in June 2011 when compared to either the normal conditions in June 2014 or in drought conditions in June 2012 (Table 6). Bottom PM concentrations for flood conditions in June 2013 are statistically greater when compared to normal conditions in June 2014 and in drought conditions in June 2012 (Figure 12, Table 6). Lower PM concentrations have previously been observed in times of low river discharge in 2007 (Cai, et al., 2015) when the discharge was equivalent to the drought conditions of June and August of 2012. The normal conditions in June 2014 are not statistically different than drought conditions in June 2012 (Figure 12, Table 6), and the normal conditions for both August of 2011 and 2013 are also not statistically different than the drought conditions of August 2012 (Figure 13, Table 6). Increased concentration of bottom PM is dominantly from resuspension of bottom material. Based on reports by Zuck (2014), the June 2012 cruise experienced significant wind throughout the week-long cruise, creating strong water column mixing. The strong mixing on this cruise would lead to increased bottom PM, through resuspension, even though this cruise was during a time of very low discharge. Resuspension of biogenic material is manifest as increases in bottom backscatter, a proxy for PM concentrations, coupled with increased bottom fluorescence and decreased dissolved oxygen, (Figure 14). In shallow waters, strong wind and waves mix the entire water column resulting in uniform backscatter values (Figure 15).

Increases in PM in surface and bottom waters with increasing river discharge using the data from June 2013 flood conditions supports Hypothesis 1. There are no statistically significant increases in PM concentrations for the June 2011 flood conditions in either the surface or the bottom waters, but there is sampling bias for the study are for this cruise, as not as many stations were sampled across the whole study site. For normal conditions, the June 2014, August 2011, and August 2013 normal conditions do not support Hypothesis 1. The river discharge between normal conditions and drought conditions for August 2011 and August 2013 compared with August 2012 are not sufficient to create a statistically significant difference in PM concentrations in either the surface or bottom waters. This suggests a threshold of river discharge increase beyond which PM concentrations increase. Flood conditions compared to normal and drought conditions meet this threshold, but normal conditions compared to drought conditions do not. Furthermore, other variable factors, such as bottom resuspension and wind and wave mixing, affect the bottom PM concentrations, so river discharge is not the sole factor in determining PM concentrations.

4.1.2 Inter-annual differences in POC concentrations with changing river discharge

The inter-annual differences in POC with river discharge are for flood versus drought conditions between June 2013 (Flood) and June 2012 (Drought) and normal versus drought conditions between August 2013 (Normal) and August 2012 (Drought)(Table 5). Surface water POC concentrations are statistically higher during the flood conditions of June 2013 compared to drought conditions in June 2012 (Figure 16, Table 5). In the August cruise comparisons, surface water POC concentrations are not statistically significantly different between normal conditions in August 2013 and drought conditions in August 2012 (Figure 16, Table 5). Surface POC concentrations are greater only for the case of very high river discharge when compared to very low river discharge. Similarly, increased POC concentrations were observed with increasing river discharge in 1990-1991 (Trefry, et al., 1994), 2000 (Wysocki, et al., 2006), 2000-2001 (Wang, et al., 2015), and in 2006-2008 (Cai, et al., 2015). In the Mississippi river plume water where concentrations of PM are greater than 50 mg/L, 98% of the material is terrestrial based, and only 2% consists of POC (Trefry, et al., 1994). Most POC in the surface waters of the Gulf of Mexico is derived from marine phytoplankton production (Duan and Bianchi, 2006). Increasing the Mississippi river input increases the nutrient load delivered to the Gulf of Mexico, which stimulates primary production and therefore increases POC concentrations of the surface waters, as observed in the results of this study.

The bottom water POC concentrations are not statistically different between the flood conditions of June 2013 compared with the drought conditions in June 2012, or the normal conditions in August 2013 compared to drought conditions in August 2012 (Figure 17, Table 6). Though more POC is produced in the surface waters with increased river discharge, the organic material is decomposed in the water column by bacteria, with very little remaining in the bottom waters.

Increased river discharge leads to an increase in surface POC concentrations in only one case (Flood vs. Drought in June), and in no case for bottom POC concentrations. Therefore, for POC, Hypothesis 1 is not supported for bottom waters and only for extreme conditions in surface waters. POC concentrations in the water column throughout the NGOM are seldom directly related to river input. Other factors influence the presence of POC in the water column, such as primary production in the surface waters and decomposition by bacteria in the water column.

4.1.3 Inter-annual differences in C:N Ratios with changing discharge

The C:N ratio indicates the state and nature of the organic material, with newly produced marine organic matter having a C:N ratio approximately equal to the Redfield Ratio of 6.6 (Redfield, et al., 1963). A primarily bacteria dominated community has C:N values below 6.6, or older, decaying organic material, with value above 6.6, and below 15, the sediment end member (Redfield, et al., 1963; Wissel, et al., 2005; Zuck, 2014). Based on results of the ^{13}C:^{15}N ratios conducted for the 2011 cruises, the low C:N ratios for flood conditions during June of 2011 may contain a large amount of bacterioplankton and potentially cyanobacteria. The high C:N values in August of 2011 are suggestive of more decayed organic material (Zuck, 2014). In the surface waters C:N ratios are statistically different during flood conditions compared with drought conditions for both June and August cruises (Figures 18, 19). The C:N ratios in bottom waters are also statistically different during higher discharge conditions when compared to lower discharge conditions for all June cruises (Figure 20), but not for the case of normal conditions of August 2011 compared to drought conditions for August 2012 (Figure 21). Compared to the Redfield Ratio, the flood cruises have lower C:N ratios, the normal cruises have a mix of low and high C:N ratios, and the drought cruises have higher C:N ratios in both the surface and the bottom waters. The lower C:N ratios during the flood cruises in both the surface and bottom waters indicate that the organic matter consists of phytoplankton, at C:N ratios of 6.6, or possibly more bacterioplankton, with C:N ratios lower than 6.6 (Zuck, 2014). As river discharge increases, the increased nutrients fuel primary production. The increase in organic material can be consumed by bacteria thereby lowering the C:N ratio. During drought conditions, primary production in the water column is not as high as during normal or flood conditions, and older and partially remineralized organic matter with higher C:N ratios are present . The C:N ratios during normal discharge cruises are centered around 6-7, close to the Redfield ratio, indicating that most of the organic matter is recently produced in the water column (Redfield, et al., 1963).

Hypothesis 1 is supported by lower C:N ratios during times of higher river discharge and higher C:N ratios during times of lower river discharge for both the surface and the bottom waters in all but one case. The lower C:N ratios during higher river discharge are potentially a mix of freshly produced phytoplankton and bacterioplankton, while the higher C:N ratios during lower river discharge conditions are more degraded organic material.

4.2. Hypothesis 2- PM and POC concentrations and C:N ratios in the surface and bottom waters are statistically different between June and August of each year 2011-2013.

4.2.1 PM concentrations

Of the three years of June and August cruises, surface and bottom water PM concentrations are statistically higher in June only in 2013 (Figure 22 and 23, Table 7 and 8). Increased PM concentrations in surface waters generally coincide with increased river discharge. No statistical difference is seen in 2012 in PM concentration in surface or bottom waters, when drought conditions existed in both June and August. Lower river discharge brings less PM to the Gulf as seen in the inter-annual variability (Figure 10). In 2013, there is a large and rapid decrease in river discharge between June and August, drastically decreasing the amount of freshwater and particulate matter emptying into the Gulf of Mexico (Figure 2), which in turn could lead to the difference in observed surface PM concentration between June and August. It is unexpected to find surface differences between June and August of 2013 and not in 2011 when there was an even larger difference in discharge between the two months. Changes in bottom PM concentrations could be related to river discharge. The lack of difference as shown in the Wilcoxon test suggests this, but the high bottom values for both June and August of 2011 near the Mississippi River (Figure 24) are more likely affected by local sediment resuspension.

The lack of statistically significant differences between surface and bottom PM concentrations between June and August of the same year does not fully support Hypothesis 2. June PM concentrations are only higher than August PM concentrations for one of the three years observed (2013), indicating that the surface and bottom PM concentrations do not decrease consistently between June and August. The biggest control on bottom PM concentrations is resuspension of sediments, which can occur during any months, including June and August, leading to variable differences in PM concentrations between the two months.

4.2.2 POC concentrations

Surface POC concentrations are statistically higher in June when compared to August in 2012 and 2013 (Figure 25, Table 7). Surface POC concentrations in the Gulf of Mexico are controlled mostly by primary production (Duan and Bianchi, 2006). The June cruises occur a month or two after the spring bloom and peak in POC in the northern Gulf of Mexico, which would be expected to create higher POC concentrations in June compared with August, as seen in 2012, with a 2.6% increase, and 2013, with a 11.4% increase (Figure 26 and 27). The August cruises take place an additional two months later than the spring bloom and POC peak occur, so POC has significantly decreased in surface waters.

The bottom POC concentrations are not statistically different in June than August in any year analyzed (Figure 28, Table 8). Increases in POC concentrations from the phytoplankton production occur in surface waters. As that POC sinks through the water column, it can be remineralized, causing up to half of the surface POC to be exported out of the surface waters where it can be consumed (Redalje, et al., 1994). The consumption of POC in the water column reduces POC in bottom waters. This is in fact observed; during no year were POC concentrations different between June and August for bottom waters.

Hypothesis 2 is supported in surface waters for both 2012 and 2013; POC concentrations are higher in surface waters in June than in August for those years. However, Hypothesis 2 is not supported for bottom POC concentrations. June cruises do have a statistically significant difference in POC concentrations when compared to August for bottom waters during 2012 and 2013.

4.2.3 C:N ratios

Surface and bottom C:N ratios are statistically different in June compared to August for two of the three years, 2011 and 2013 (Figure 29, Tables 7 and 8). Surface and bottom water C:N ratios for August of 2011 and 2013 have higher C:N ratios than June. The June cruises are closer in time to the spring bloom, so a majority of the organic matter in the surface waters is recently produced phytoplankton detritus or bacterioplankton, so the C:N ratio is lower with values mostly between 5 and 7 (Figure 29) for both June of 2011 and 2013. Organic matter in August is older and more remineralized, leading to higher C:N ratios with values generally between 7-10 (Figure

29). While much of the August organic matter is remineralized, the lower range of the C:N ratio also indicated that the material still has some fresher phytoplankton detritus.

In 2012, there is no statistical difference in the C:N ratios for June to August in surface or bottom waters (Figures 29 and 30, Table 7 and 8). Due to the low discharge during 2012, the phytoplankton bloom was smaller in both magnitude and areal extent compared with the other years sampled that have higher river discharge. Because primary production was low for the entire sampled season, as evident by the lowest POC concentrations in 2012 when compared to 2011 or 2013, less fresh phytoplankton detritus is present, leading to more of the organic matter being remineralized, resulting in higher C:N ratios in both surface and bottom waters in 2012.

Bottom C:N ratios are statistically higher in June compared to August for 2011 and 2013; the years with highest discharge. The June-August C:N ratios are not different for 2012 (Figure 30, Table 8). The low values from June of 2011 and 2013 are due to phytoplankton, for values near 6.6, and by bacterioplankton, values lower than 6.6. The higher C:N values for August of 2011 are due to more degraded organic material (Zuck, 2014). The higher values of bottom C:N ratios for June and August of 2012 and 2013 when compared to 2011 are representative of more degraded organic material. The same statistical differences are reflected in the surface waters. As the material present in the surface sinks through the water column, the ratios stay constant.

Surface and bottom water C:N ratios support Hypothesis 2 that C:N ratios are different between June and August for the years when June is a flood condition (2011 and 2013). In the 2012 drought conditions, the overall amount of production was very low for both June and August, and the C:N ratios for the surface and the bottom waters were not statistically different.

4.3 Hypothesis 3- Increased river discharge supports an increase in concentrations of PM and POC at the surface near the freshwater source, but not in the outer regions of the shelf.

4.3.1 Surface PM for "near source" areas

The Mississippi, Terrebonne, and Atchafalaya Boxes are defined as areas near the river sources, and the Sabine Box and the Shelf Box are defined as far from source areas (Figure 3). Of the near source areas, the Atchafalaya Box had the strongest correlation of river source discharge with surface backscatter (a proxy for PM concentrations) averaged along the Acrobat lines (Figure 31), but the ranges of both variables are small. The Atchafalaya River is the nearest river source to the Atchafalaya Box. There are moderate correlations of surface backscatter and Mississippi River discharge in the Mississippi Box (Figure 32) and mild correlations in the Terrebonne Box, using discharge of the combined Mississippi and Atchafalaya Rivers (Figure 33). Suspended particulate material has been observed by others to settle out within 5 km from the river mouth, with a decreasing amount observed as far as 70 km from the river mouth (Trefry, et al., 1994). This supports the expected finding that the boxes closest to a freshwater source, such as the Mississippi Box and Atchafalaya Box, have the strongest correlations of surface water PM with river discharge. The Terrebonne Box is even further from the mouth of both the Mississippi and Atchafalaya Rivers, with parts of the Terrebonne Box being as far as 150 km from both rivers. This distance explains the reduced correlation of PM concentrations with river discharge. As PM enters the Gulf of Mexico from a river, the material flocculates and settles out. As the distance from the river source increases, more material has settled out of the surface waters, affecting the overall trend for the boxes with greater distances from the source. Additionally, as river discharge increases, the distance the PM in the surface waters can travel within the river plume increases. In Trefry, et al. (1994), the higher discharge in February 1991 had total suspended material up to 3 mg/L at distances as far as 30-70 km from the mouth of the Mississippi River, whereas during the lower discharge in July 1990, total suspended material of 3 mg/L was measured at distances only 15-30 km from the mouth of the Mississippi River. In the analysis of this hypothesis, the river discharge is not taken into account, so the effects of both drought cruises and flood cruises are combined.

Overall, Hypothesis 3 is supported for areas very close to the source (Mississippi and Atchafalaya Box), but is not supported for the Terrebonne Bay Box, part of which is 150 km from the source.

4.3.2 Surface PM for "far from source" areas

For the far from source areas, the Sabine Box had a slope of almost zero, which is insignificant and will not be analyzed further. The backscatter for the far from source area, Sabine Box, does support Hypothesis 3, indicating that there is no correlation between far from source areas and increased surface PM concentrations.

4.3.3 Surface POC for "near source" areas

The strongest correlations of surface POC and river discharge were from the Mississippi and Atchafalaya Boxes (Figures 34 and 35). The areas near the river source receive a large supply of nutrients, which fuels primary production in the surface water, increasing POC in those areas (Trefry, et al., 1994). Furthermore, the correlation of PM and POC concentrations (Figure 36) shows that there is a moderately strong relationship between the amount of PM in the waters and the amount of POC in the waters. Wang, et al. (2004) also observed higher POC concentrations in water directly near the Mississippi and Atchafalaya River mouths in 2000 and 2001, trends also shown here for the near source Mississippi and Atchafalaya Boxes. The distance to the source explains the lower correlation found in the Terrebonne Box (Figure 37) as it is located further from both the Mississippi and Atchafalaya Rivers than the Mississippi and Atchafalaya Boxes.

The Mississippi Box and a small area of the Atchafalaya Box are located in Zone 1 of Dale et. al. (2010) (Figure 1), the zone closest to the river mouths and most influenced by river discharge. While freshwater discharge is a source of terrestrial POC in the Gulf of Mexico, it represents only a small amount, about 2%, of the POC in the Gulf of Mexico (Trefry, et al., 1994, Duan and Bianchi, 2006; Wysocki, et al., 2006). Much of the POC (and PM) derived from the terrestrial sources flocculates out close to the river mouth (Trefry, et al., 1994).

The Atchafalaya and Terrebonne Boxes are located mostly in Zone 2, or the "Green Zone" (Dale, et al., 2010; Rowe and Chapman, 2002) (Figure 1). This zone is characterized by high primary production, creating a green color in surface waters due to a dramatic increase in the POC concentration due to phytoplankton. Surface POC in the Terrebonne Box and a majority of the Atchafalaya Box is almost entirely from marine plankton production.

Overall, there is a mild to moderately strong with surface POC concentrations and river discharge in the areas near the river sources which supports Hypothesis 3.

4.3.4 Surface POC for "far from source" areas

The far from source boxes are the Sabine Box and the Mid-Shelf Box (Figure 3). The slope for the Mid-Shelf Box is almost zero. The Sabine Box shows a moderate positive correlation of surface POC concentrations with the Mississippi and Atchafalaya River discharges (Figure 38). While the Sabine Box is classified as far from the Mississippi and the Atchafalaya River sources, some river water may be transported along coast to the Sabine area. The moderate correlation between POC concentrations and combined river discharge suggests the along-slope transport affects the Sabine area. There are also many small lakes (Lake Sabine) and other tributaries that discharge into the Gulf of Mexico near the Sabine Box, but the discharge from these sources are insignificant compared to the combined Mississippi and Atchafalaya River outflows, but are much closer. Furthermore, some primary production could contribute to the amount of POC observed in the surface waters in the area of the Sabine Box (Duan and Bianchi, 2006).

The surface POC shows moderate correlation with river discharge for one far from source area (Sabine Box) and no correlation for the second area (Mid-Shelf Box).

Since both areas were expected to have no correlation, these data do not fully support the second part of Hypothesis 3 for surface POC concentrations.

4.4. Hypothesis 4- Changes in river discharge have little impact on concentrations of PM in bottom waters, either near the river source or in regions away from the river source.

For bottom backscatter, a proxy for PM concentrations, all three near-shore boxes, Mississippi, Terrebonne, and Atchafalaya, as well as the far from source box, Sabine, had slopes with a value near zero. Therefore, the bottom PM concentrations from the Acrobat data are considered to have no significant correlation. Resuspension controls a majority of the bottom PM concentrations, not river discharge, so the proximity to the river source plays no role on the bottom PM concentrations for the areas on which this study focused. The results support Hypothesis 4; the distance to freshwater sources has little impact on the bottom backscatter values either near the source or far from the source.

5. CONCLUSIONS

PM concentrations in surface waters increased with higher river discharge only during one flood period compared to a drought and normal period, showed an increase in concentration in months closer to peak discharge (June) compared with later (August) in only one out of three years, and consistently showed increases with river discharge in areas closer to the freshwater sources (Mississippi, Atchafalaya, and Terrebonne Boxes). Bottom PM concentrations increased with higher river discharge during a flood event when compared to a drought or normal event, indicated no difference in concentration in months closer to peak discharge (June) compared with later (August) except in 2013, and showed no increase with distance from the riverine source. PM concentrations in the surface waters are influenced by the river inputs, whereas PM concentrations in the bottom waters are due to sediment resuspension potentially caused by currents and waves.

POC concentrations in surface waters increase with increased river discharge during flood conditions, in months closer to peak discharge (June) compared with later (August), and in areas close to river input. POC concentrations in the bottom waters do not show a difference with increase in river discharge or during months closer to peak discharge (June) compared with later (August). POC in the surface waters is dominated by phytoplankton production with only ~2% of POC coming from terrigenous sources (Trefry, et al., 994). Since an increase in river discharge also increases the amount of nutrients in the surface waters, the amount of primary production of POC increases. In surface waters, June is closer in time to the spring bloom than August, so surface POC in June is greater due to increased primary production. However, that POC is grazed and mostly remineralized as it sinks. Therefore, the bottom POC concentrations are not statistically different with discharge throughout the entire study

The processes of the northern Gulf of Mexico are very dynamic. While PM and POC display changes due to river discharge and proximity to riverine source, these are only two of the possible controls of variability of PM and POC in the Gulf of Mexico.

REFERENCES

Allison, Mead A., Gail C. Kineke, Elizabeth S. Gordon, Miguel A. Goni. 2000. Development and reworking of a seasonal flood deposit on the inner continental shelf off the Atchafalaya River. *Continental Shelf Research* 20: 2267-2294.

Allison, Mead, A., Brian M. Vosburg, Michael T. Ramiez, and Ehab A. Meselhe. 2013. Mississippi River channel response to the Bonnet Carré Spillway opening in the 2011 flood and its implications for the design and operation of river diversions. *Journal of Hydrography* 477: 104-118.

Bianchi, R. S., S. F. DiMarco, Jr J. H. Cowan, R. D. Hetland, P. Chapman, J. W. Day, and M. A. Allison. 2010. The science of hypoxia in the northern Gulf of Mexico: A review. *Science of the Total Environment* 408 (7): 1471-1484.

Brewer, Devon D. "Understanding Statistics." *University of Washington*, 2003. Accessed 2016. http://faculty.washington.edu/ddbrewer/s231/s231regr.htm.

Cai, Yihua, Laodong Guo, Xuri Wang, and George Aiken. 2015. Abundance, stable isotopic composition, and export fluxes of DOC, POC, and DIC from the Lower Mississippi River during 2006-2008. *Journal of Geophysical Research: Biogeosciences* 120: 2273-2288.

Cochran, E. M. 2013. The role of particulate matter in the development of hypoxia on the Texas-Louisiana shelf. M.S. Thesis: Texas A&M University.

Cochrane, J. D., and F. J. Kelly. 1986. Low-frequency circulation on the Texas-Louisiana continental shelf. *Journal of Geophysical Research* 91 (C9): 10645-10659.

Coleman, J. M., and L. D. Wright. 1975. Modern river deltas: variability of processes and sand bodies. *Deltas. Models for Exploration*: 99-149.

Corbett, D. Reide, Brent McKee, and Dan Duncan. 2004. An evaluation of mobile mud dynamics in the Mississippi River deltaic region. *Marine Geology* 209: 91-112.

Dale, V. H., C. Kling, J.L. Meyer, J. Sanders, H. Stallworth, T. Armitage, D. Wangsness, T.S. Bianchi, A. Blumberg, W. Boynton, D.J. Conley, W. Crumpton, M.B. David, D. Gilbert, R.W. Howarth, R. Lowrance, K. Mankin, J. Opaluch, H. Paerl, K. Reckhow, A.N. Sharply, T.W. Simpson, C. Synder, and D. Wright. 2010. Hypoxia in the northern Gulf of Mexico. New York, Springer, Springer Series on Environmental Management.

Diaz, Robert J. and Rutger Rosenberg. 1995. Marine benthic hypoxia: a review of its ecological effects and the behavioural responses of benthic macrofauna. *Oceanography and Marine Biology: an Annual Review* 33: 245-303.

Diaz, Robert J., and Rutger Rosenberg. 2011. Introduction to environmental and economic consequences of hypoxia. *Water Resources Development* 27 (1): 71-82.

DiMarco, Steven F., P. Chapman, Nan Walker, and Robert D. Hetland. 2010. Does local topography control hypoxia on the eastern Texas-Louisiana shelf? *Journal of Marine Systems* 80: 25-35.

DiMarco, S. F. 2013 Mechanisms Controlling Hypoxia: Cruise Overview. Texas A&M University: College of Geosciences.

Duan, Shutwang and Thomas S. Bianchi. 2006. Seasonal changes in the abundance and composition of plant pigments in particulate organic carbon in the lower Mississippi and Pearl Rivers. *Estuaries and Coasts* 28 (3): 427-442.

Harper, D. E., Jr., L. D. McKinney, R. R. Salzer, and R. J. Case. 1981. The occurrence of hypoxic bottom water off the upper Texas coast and its effects on the benthic biota. *Contributions in Marine Science* 24: 53-79.

Hetland, Robert D., and Steven F. DiMarco. 2008. How does the character of oxygen demand control the structure of hypoxia on the Texas-Louisiana continental shelf? *Journal of Marine Systems* 70: 49-62.

Hopkinson, Charles, S. Jr., and Erik Smith M. 2005. Estuarine respiration: An overview of benthic, pelagic, and whole system respiration. In *Respiration in Aquatic Ecosystems.*, eds. Paul del Giorgio, Peter Williams. Oxford University Press, Inc., New York. 122-146.

JGOFS Report No. 19. 1996. Protocols for the Joint Global Ocean Flux Study (JGOFS) Core Measurements, (http://ijgofs.whoi.edu/Publications/Report_Series/JGOFS_19.pdf).

Lehrter, J. C., M. C. Murrell, and J. C. Kurtz. 2009. Interactions between freshwater input, light, and phytoplankton dynamics on the Louisiana continental shelf. *Continental Shelf Research* 29: 1861-1872.

"Mississippi Mile Markers and Speed." *Outdoor Adventures*. Accessed May 23, 2016. http://bucktrack.com/Missisippi_River_Canoe_Speed.html

"Mississippi River Facts." *National Park Service.* Accessed May 23, 2016. https://www.nps.gov/miss/riverfacts.htm.

Milliman, John D. and Robert H. Meade. 1983. World-wide delivery of river sediment to the oceans. *The Journal of Geology* 91 (1): 1-21.

Neill, Ciara F., and Mead A. Allison. 2005. Subaqueous deltaic formation on the Atchafalaya shelf, Louisiana. *Marine Geology* 214: 411-430.

Obenour, Daniel R., Donald Scavia, Nancy N. Rabalais, Anna M. Michalak, and Anna M. Michalak. 2013. Retrospective analysis of midsummer hypoxic area and volume in the northern gulf of Mexico, 1985-2011. *Environmental Science and Technology* 47: 9808-9815.

Osterman, Lisa E., Richard Z. Poore, Peter Swarzenski W., and R. Eugene Turner. 2005. Reconstructing a 180 yr record of natural and anthropogenic induced low-oxygen conditions form Louisiana continental shelf sediments. *Geology* 33 (4): 329-332.

Rabalais, Nancy N., R. Eugene Turner, and Donald Scavia. 2002. Beyond science into policy: Gulf of Mexico hypoxia and the Mississippi river. *Bioscience* 52 (2): 129-142.

Rabalais, Nancy N., R. Eugene Turner, and William J. Wiseman Jr. 2002. Gulf of Mexico hypoxia, a.k.a "the dead zone". *Annual Review of Ecology and Systematics* 33: 235-263.

Rabalais, Nancy N., R. E. Turner, B. K. Sen Gupta, D. F. Boesch, P. Chapman, and M. C. Murrell. 2007. Hypoxia in the Northern Gulf of Mexico: Does the science support the plan to reduce, mitigate, and control hypoxia? *Estuaries and Coasts* 30 (5): 753-772.

Rabalais, Nancy N., R. Eugene Turner, Robert J. Diaz, and Dubravko Justic. 2009. Global change and eutrophication of coast waters. *Ices Journal of Marine Science* 66: 1528-1537.

Redfield, A. C., B. H. Ketchum, and F. A. Richard. 1963. The influence of organisms on the composition of seawater. Wiley: New York, New York, *The Sea*.

Redalje, D. G., S. E. Lohrenz, G. L. Fahnensteil. 1994. The relationship between primary production and the vertical export of particulate organic matter in a river-impacted coastal system. *Estuaries* 17: 829-838.

Rowe, G. and P. Chapman. 2002. Continental Shelf Hypoxia: Some Nagging Questions. *Gulf of Mexico Science* 2: 153-160.

Rowe, Gilbert T. and Jody W. Deming. An alternative view of the role of heterotrophic microbes in the cycling of organic matter in deep-sea sediments. *Marine Biology Research* 7 (7): 629-636.

Stramski, D., R. A. Reynolds, S. Kaczmarek, M. R. Lewis, R. Rottgers, A. Sciandra, M. Stramska, M. S. Twardowski, B. A. Franz, and H. Claustre. 2008. Relationships between the surface concentrations of particulate organic carbon and optical properties in the eastern South Pacific and eastern Atlantic Oceans. *Biogeosciences* 5: 171-201.

Thronson, A. and A. Quigg. 2008. Fifty-five years of fish kills in coast Texas. *Estuaries and Coasts* 31: 802-813.

Trefry, John H., Simone Metz, Terry A. Nelson, Robert P. Trogine, and Brian J. Eadie. 1994. Transport of particulate organic carbon by the Mississippi River and its fate in the Gulf of Mexico. *Estuaries* 17 (4): 839-849.

Turner, R. Eugene and Nancy N. Rabalais. 1991. Changes in Mississippi River water quality this century. *BioScience* 41 (3): 140-147

USGS. 2016. USGS 07374000 Mississippi at Baton Rouge, LA.

USGS. 2016. USGS 07381490 Atchafalaya River at Simmesport, LA.

Wainright, S. C., and C. S. Hopkinson Jr. 1997. Effects of sediment resuspension on organic matter processing in coastal environments: A simulation model. *Journal of Marine Systems* 11: 353-368.

Wang, Xu-Chen, Robert F. Chen, and George B. Gardner. 2004. Sources and transport of dissolved and particulate organic carbon in the Mississippi River estuary and adjacent coastal waters of the northern Gulf of Mexico. *Marine Chemistry* 89: 241-256.

Wiseman, Wm J., N. N. Rabalais, R. E. Turner, S. P. Dinnel, and A. MacNaughton. 1997. Seasonal and interannual variability within the Louisiana coastal current: Stratification and hypoxia. *Journal of Marine Systems* 12: 237-248.

Wissel, Bjorn, Arian Gace, and Brian Fry. 2005. Tracing river influences on phytoplankton dynamics in two Louisiana estuaries. *Ecology* 86 (10): 2751-2762.

Wysocki, Laura A., Thomas S. Bianchi, Rodney T. Powell, and Nina Reuss. 2006. Spatial variability in the coupling of organic carbon, nutrients, and phytoplankton pigments in surface waters and sediments of the Mississippi River plume. *Estuarine, Coastal, and Shelf Science* 69: 47-63.

Xu, Kehui, Courtney K. Harris, Robert D. Hetland, and James M. Kaihatu. 2011. Dispersal of Mississippi and Atchafalaya sediment on the Texas-Louisiana shelf: Model estimates for the year 1993. *Continental Shelf Research* 31: 1558-1575.

Zhang, Youcheng. 1997. Sedimentation and Resuspension Across the Central Louisiana Inner Shelf. PhD Dissertation: Texas A&M University.

Zuck, N. A. 2014. The relationships of particulate matter and particulate organic carbon with hypoxic conditions along the Texas-Louisiana shelf. M.S. Thesis: Texas A&M University.

APPENDIX A

FIGURES

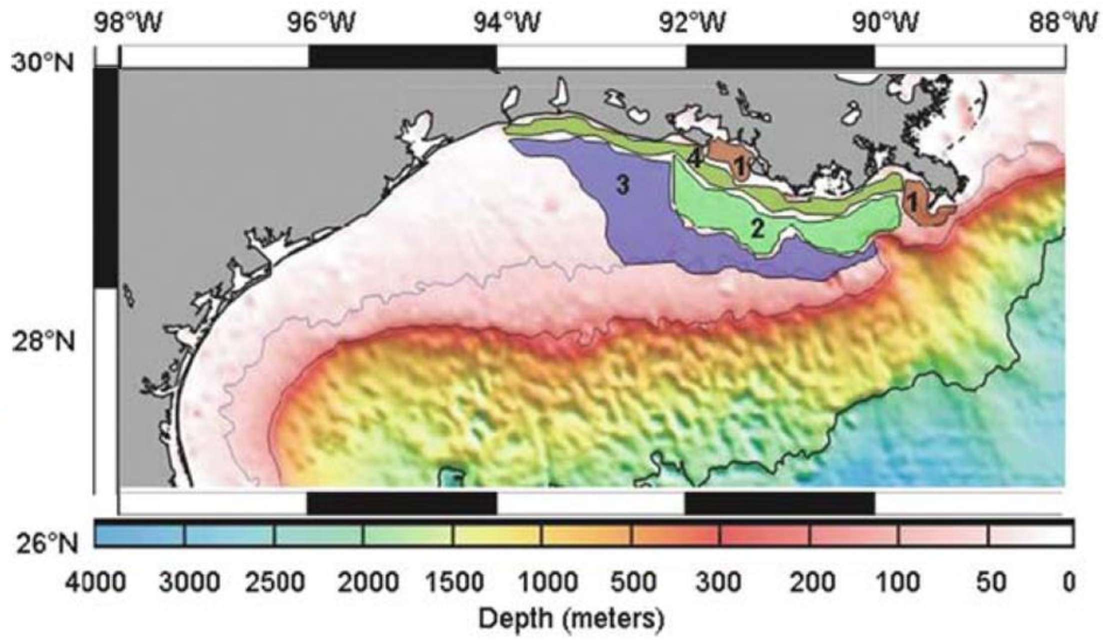


Figure 1: Bathymetric map of the Northern Gulf of Mexico showing four zones where different process influence hypoxia (Adapted from Dale, et al., 2010). See text for explanation.

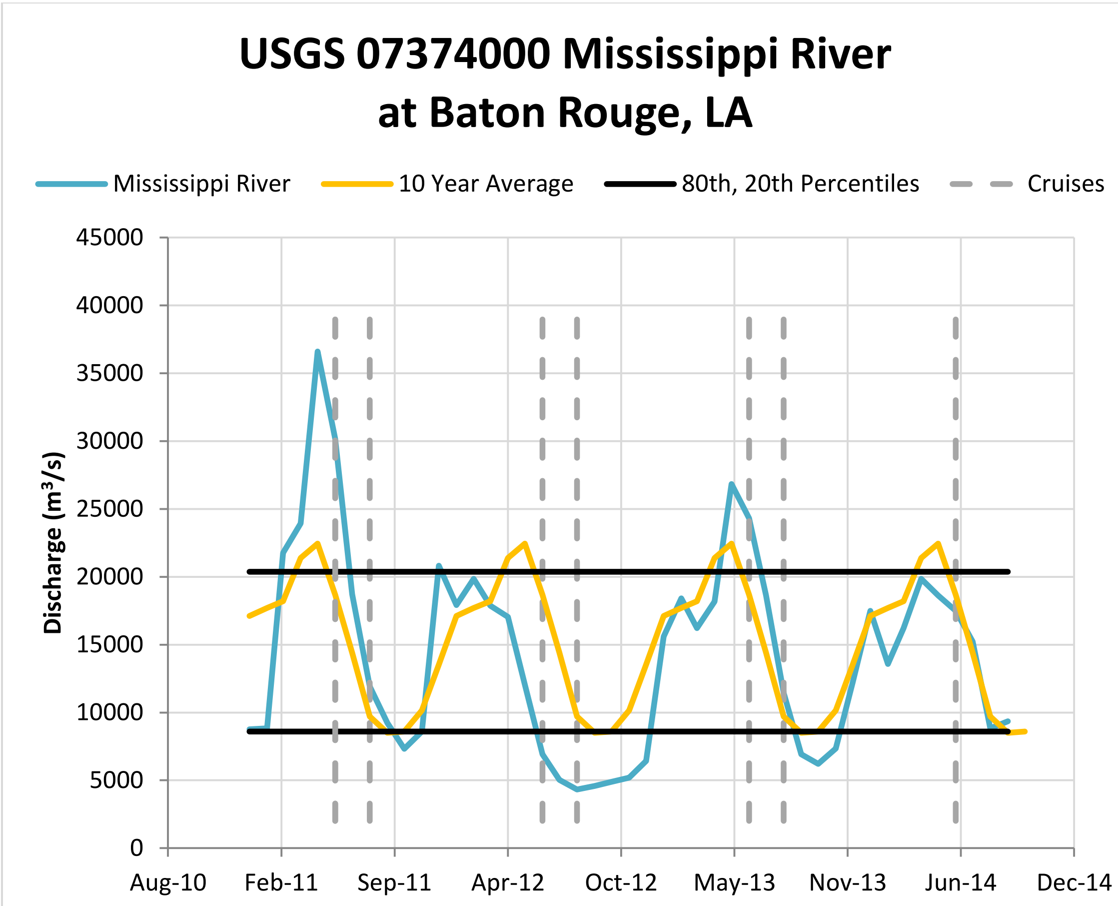


Figure 2: Mississippi River daily discharge (Blue) from January 2011 through September 2014 and the mean monthly discharge (averaged over 10 years: 2004-2014 - Orange), measured at USGS Station 07374000 at Baton Rouge, LA (USGS, 2015). Vertical gray lines from left to right are June and August of 2011, June and August of 2012, June and August of 2013, and June of 2014. The black horizontal lines are the 20th and 80th percentile of the mean monthly discharge for the same 10 year period, setting the thresholds for flood or drought, according to methods used by the US Drought Monitor System Classification.

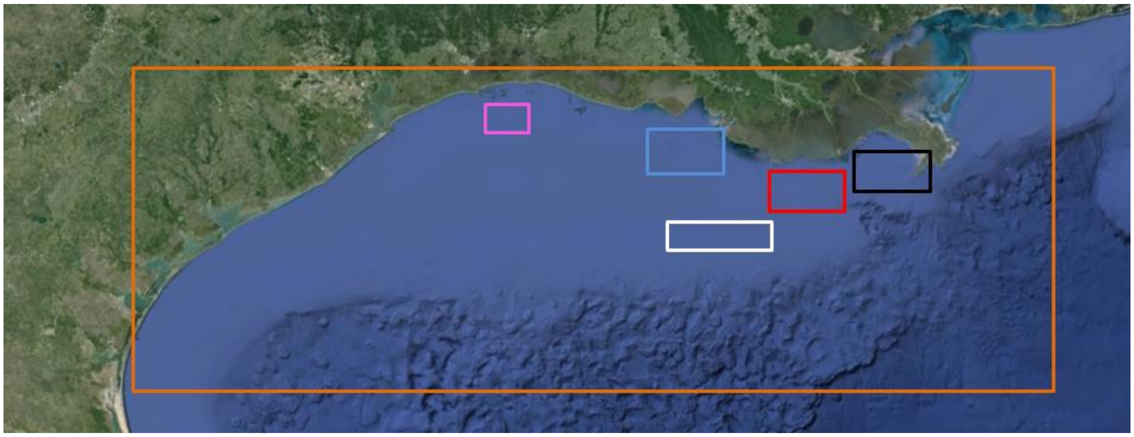


Figure 3: Satellite image of approximate areas sampled. The Northern Gulf of Mexico Box (NGOM Box) is outlined in the orange box. Analyzed areas within the NGOM Box are the Mississippi Box (black), the Terrebonne Box (red), the Atchafalaya Box (blue), the Sabine Box (pink), and the Mid-Shelf Box (white). Image courtesy of Google Earth (2015).

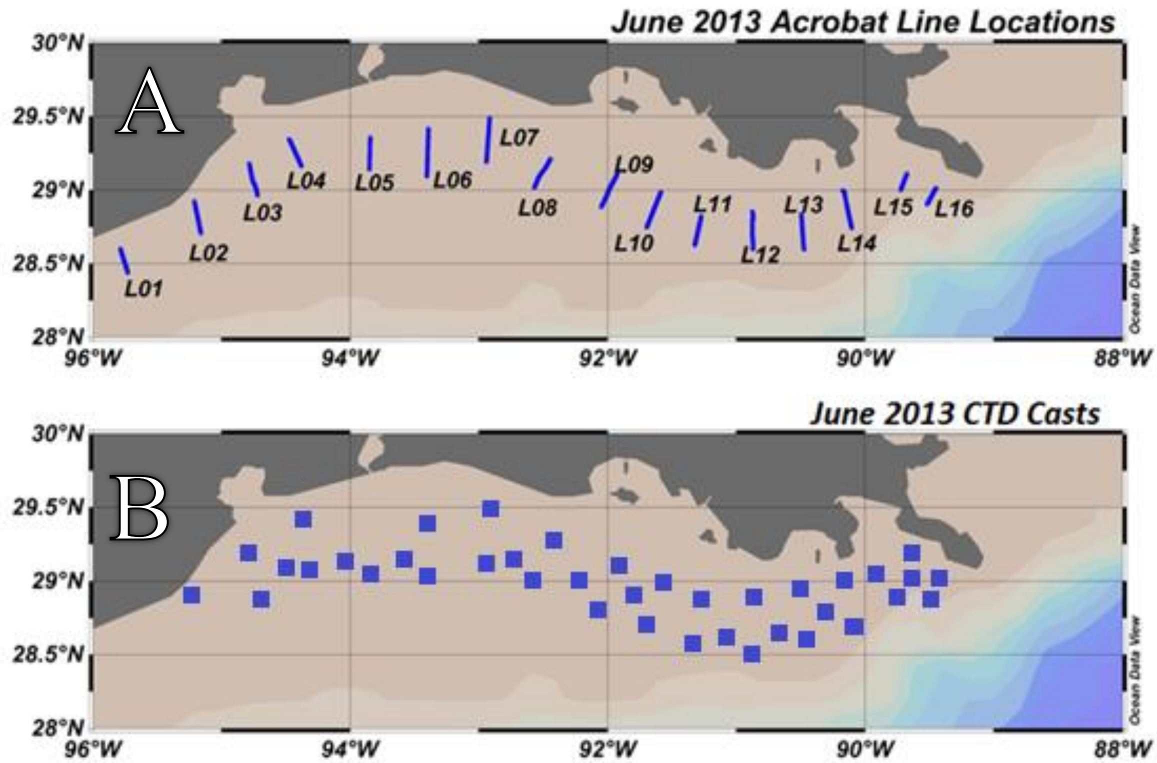


Figure 4: Acrobat lines (A) and CTD casts (B), where surface and bottom bottle samples were taken for June 2013. All cruises followed a similar sampling scheme, but some Acrobat lines or CTD casts were not able to be taken due to malfunctions and sea conditions. Image adapted from Zuck (2014).

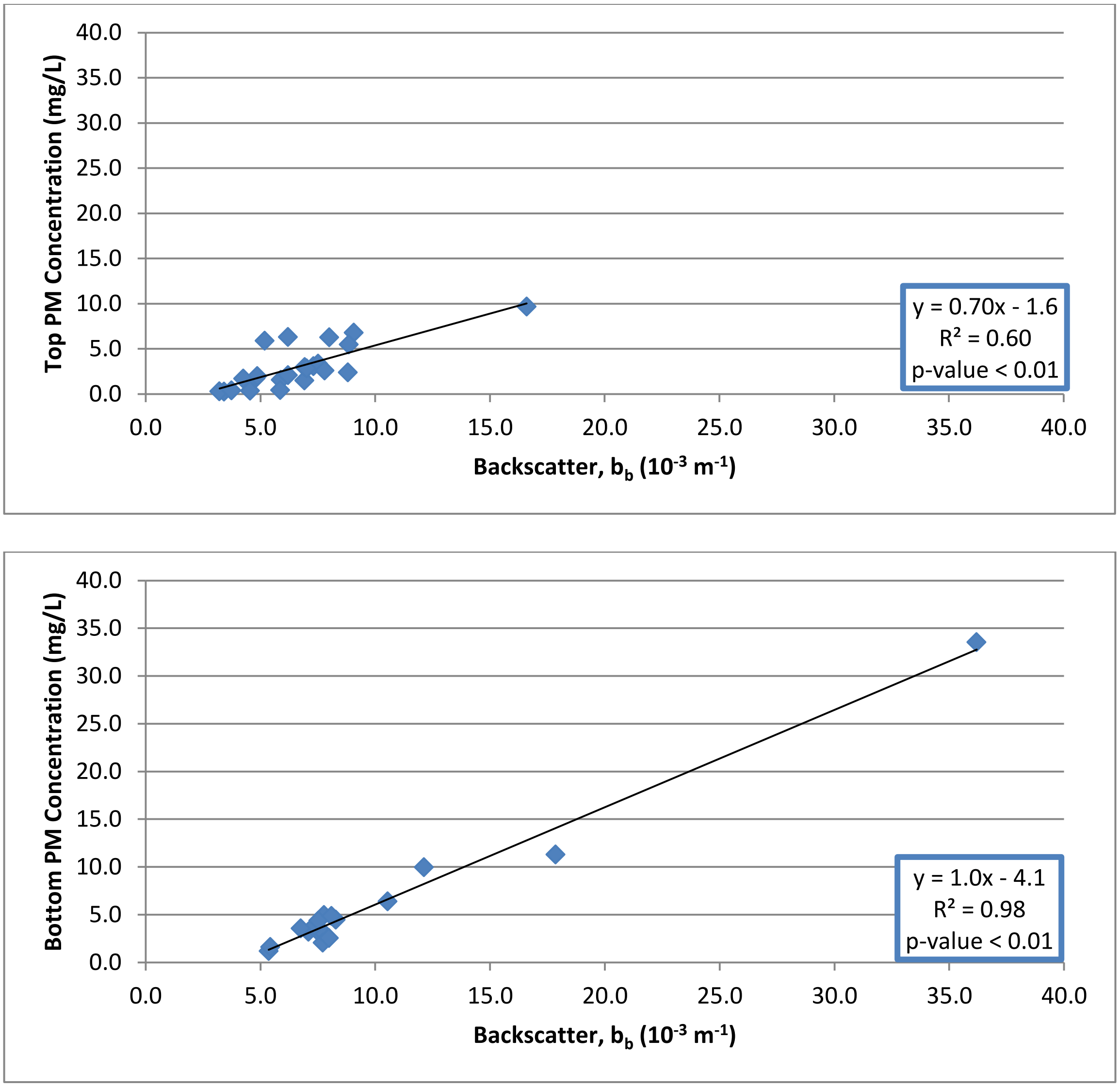


Figure 5: Top and bottom PM concentrations from bottle samples vs backscatter values from CTD data for August 2011. Backscatter is used as a proxy for PM concentrations. A summary of linear regression from bottle PM concentrations vs CTD backscatter for each cruise is located in Table 4.

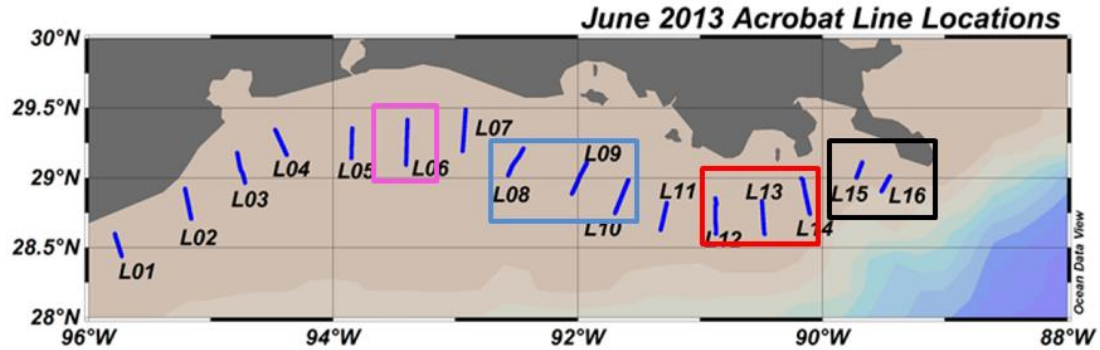


Figure 6: Acrobat lines for June 2013. All cruises followed a similar sampling scheme, but some Acrobat lines were not able to be taken due to malfunctions and sea conditions. Boxes indicate areas selected for further analysis and include the Mississippi Box (black), Terrebonne Box (red), Atchafalaya Box (blue), and the Sabine Box (pink). Image adapted from Zuck (2014).

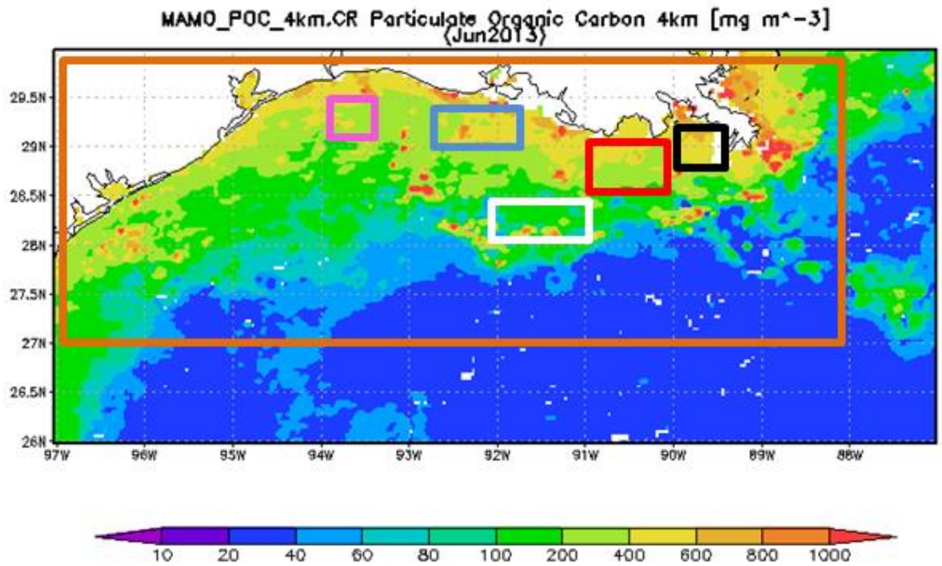


Figure 7: A map of the northern Gulf of Mexico from satellite data for POC concentrations for the Mississippi Box (black), the Terrebonne Box (red), the Atchafalaya Box (blue), the Sabine Box (pink) the Mid-Shelf Box (white), and the NGOM Box (orange).

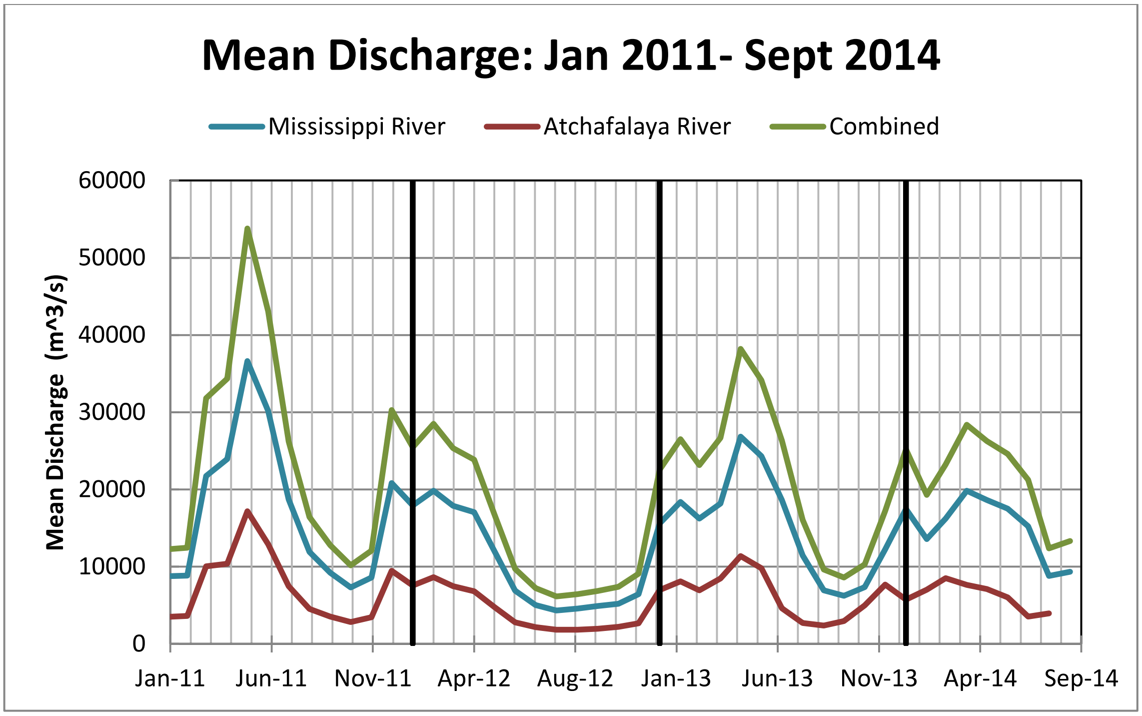
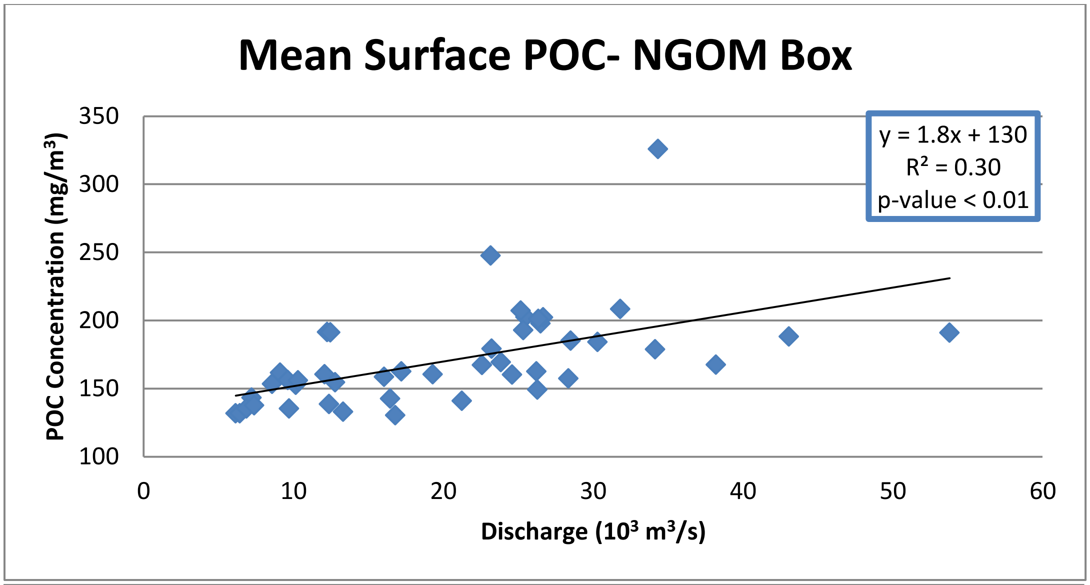


Figure 8: Monthly discharge for the Mississippi River (Gauging Station USGS 07374000), the Atchafalaya River (Gauging Station USGS 07381490), and the combined Atchafalaya and Mississippi River discharge. There are no data for July 2013 for the Atchafalaya River discharge; the combined data for July 2013 is the mean of June and August for the Atchafalaya in 2013. The combined river discharge is used for the comparisons with discharge conditions within Sabine Box, the Terrebonne Box, and the Mid-Shelf Box. The black vertical lines are January 1st of each year.



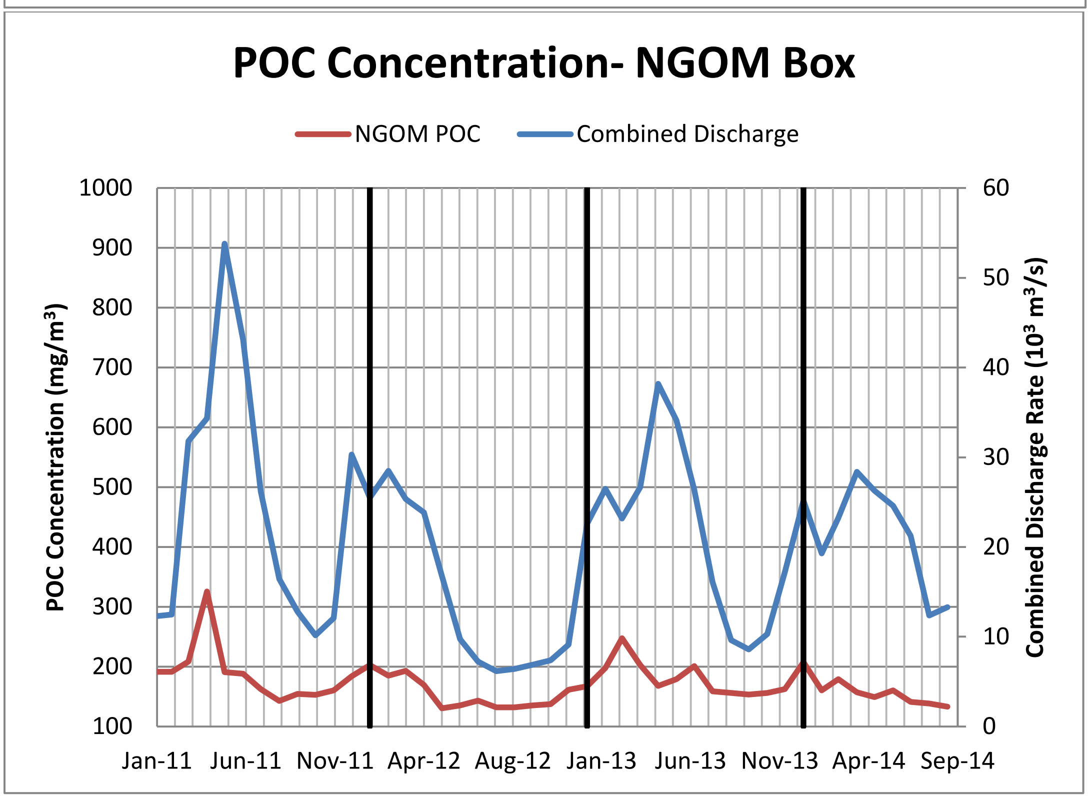
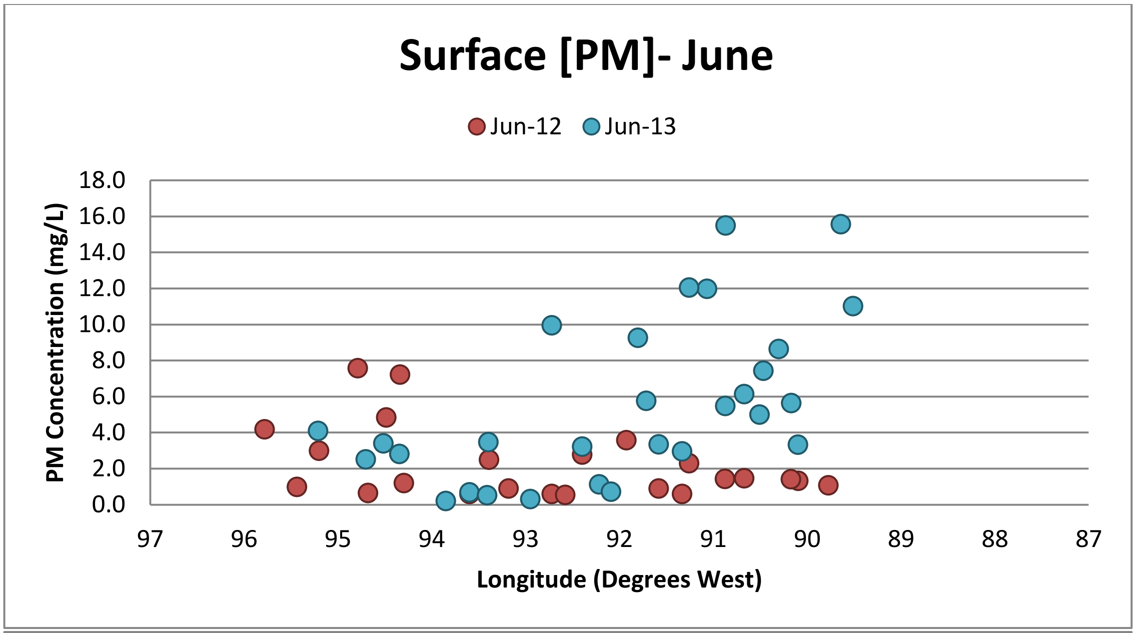


Figure 9: Monthly mean POC concentrations from satellite data in the Northern Gulf of Mexico (NGOM) Box and monthly mean river discharge of the combined Mississippi and Atchafalaya Rivers shown as a scatter plot (upper) and time series (lower) from January 2011 to September 2014. Black vertical lines represent January 1st.



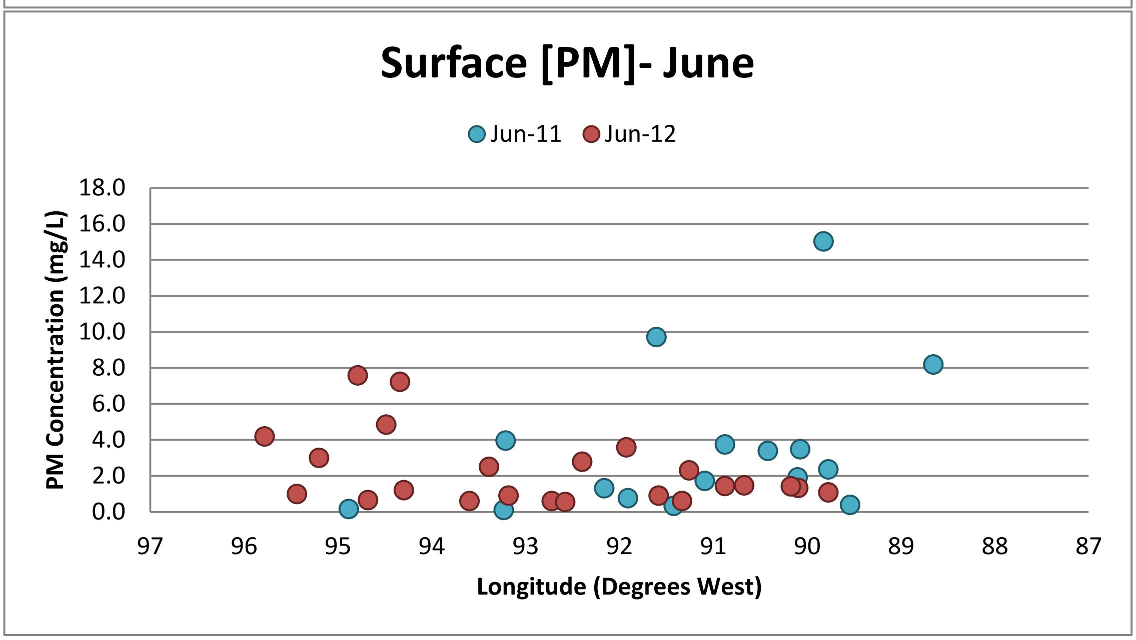


Figure 10: Top panel: surface PM concentrations for statistically different conditions: flood conditions (June 2013) vs. drought conditions (June 2012). Bottom panel: surface PM concentrations for conditions that are not statistically different: flood conditions (June 2011) vs. drought conditions (June 2012).

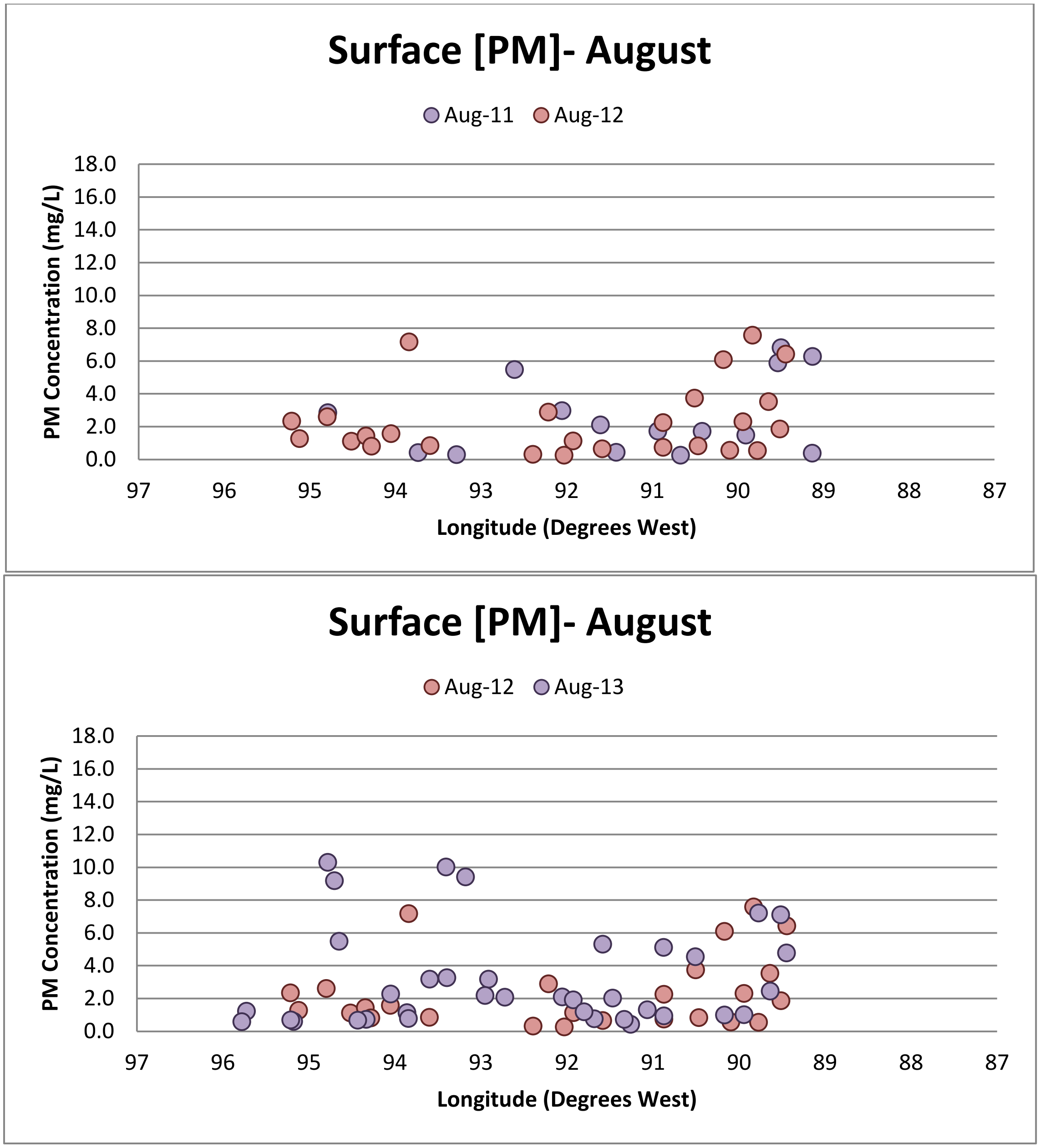


Figure 11: Top panel: surface PM concentrations for conditions that are not statistically different: normal conditions (August 2011) vs. drought conditions (August 2012).
Bottom panel: surface PM concentrations for conditions that are not statistically different: normal conditions (August 2013) vs. drought conditions (August 2012).

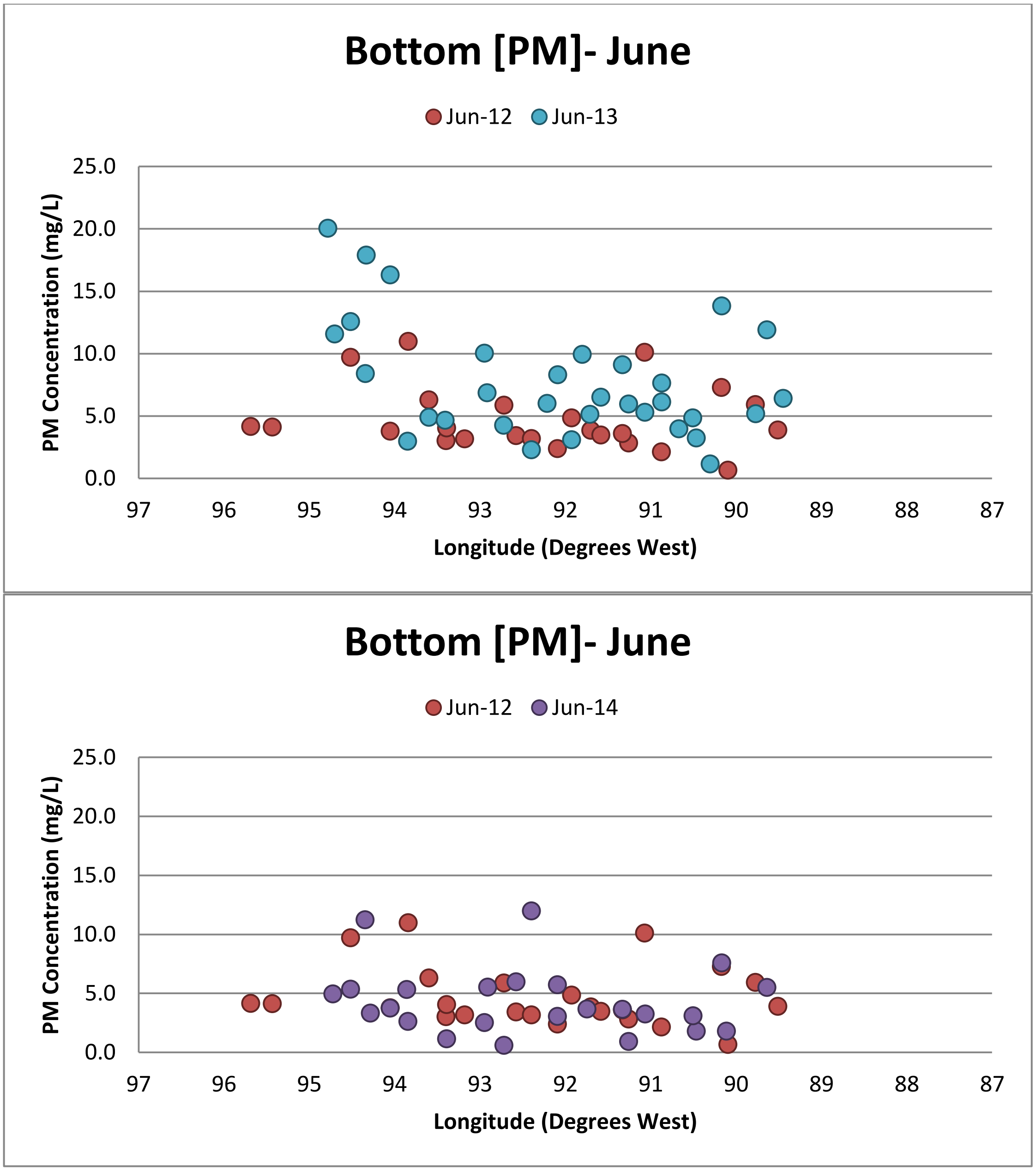
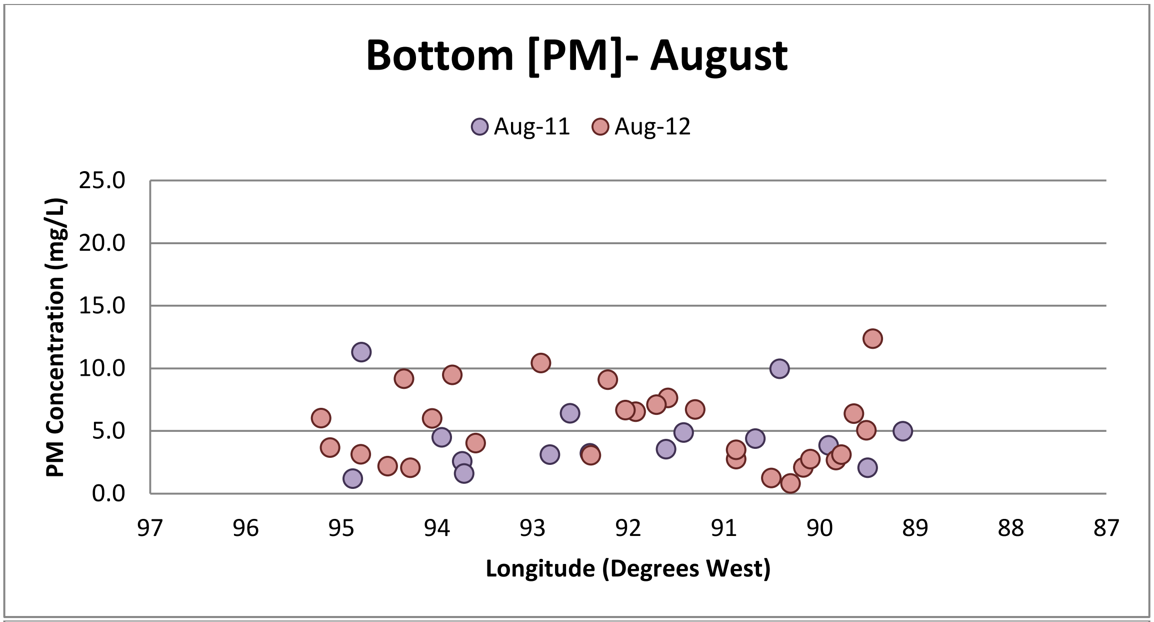


Figure 12: Top panel: bottom PM concentrations for statistically different conditions: flood conditions (June 2013) vs. drought conditions (June 2012). Bottom panel: bottom PM concentrations for conditions that are not statistically different: normal conditions (June 2014) vs. drought conditions (June 2012).



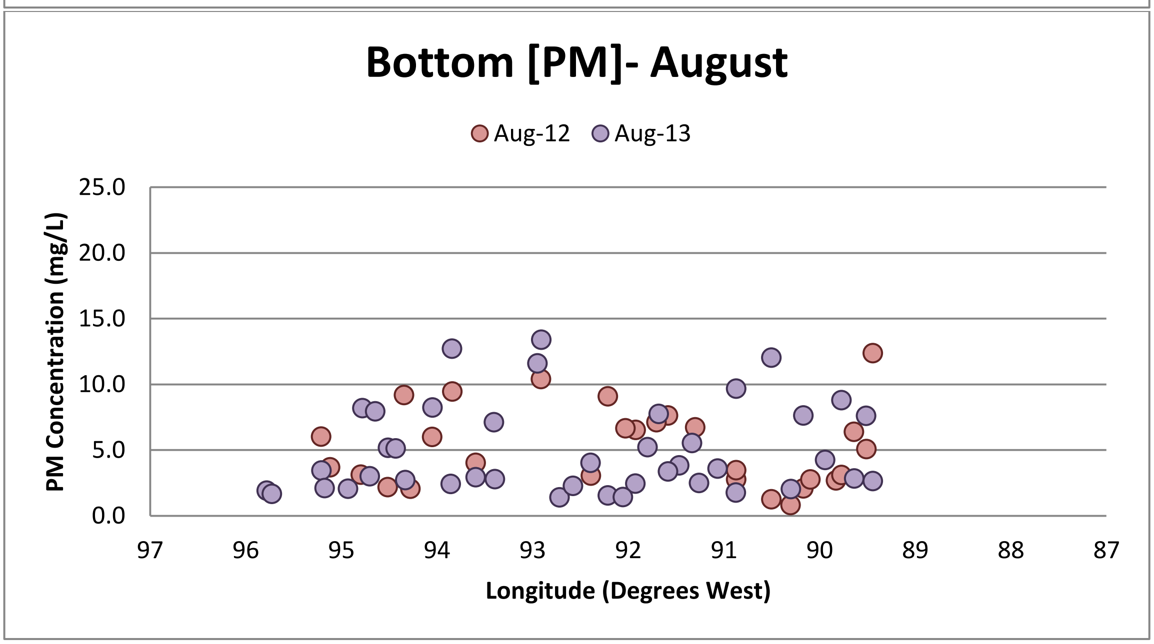


Figure 13: Top panel: bottom PM concentrations for conditions that are not statistically different: normal conditions (August 2011) vs. drought conditions (August 2012).
Bottom panel: bottom PM concentrations for conditions that are not statistically different: normal conditions (August 2013) vs. drought conditions (August 2012).

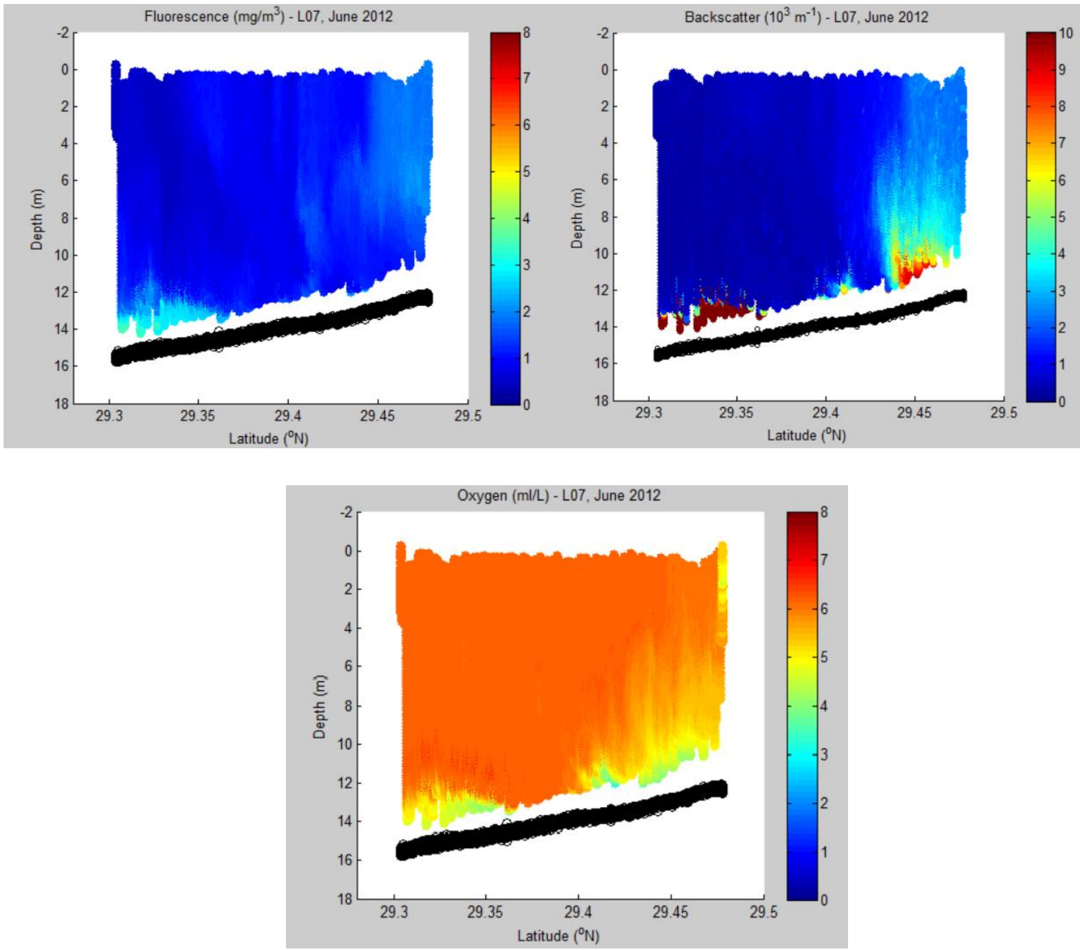


Figure 14: Line L07 for June 2012 from Acrobat data. The left panel is Chl fluorescence along line L07 and the right panel is backscatter from line L07. The center panel is dissolved oxygen along line L07. The increased bottom backscatter at depths of 13-14 meters is likely due to bottom resuspension.
Because there is also increased fluorescence and decreased dissolved oxygen, in situ production is not the cause of the increased fluorescence, but bottom resuspension is.

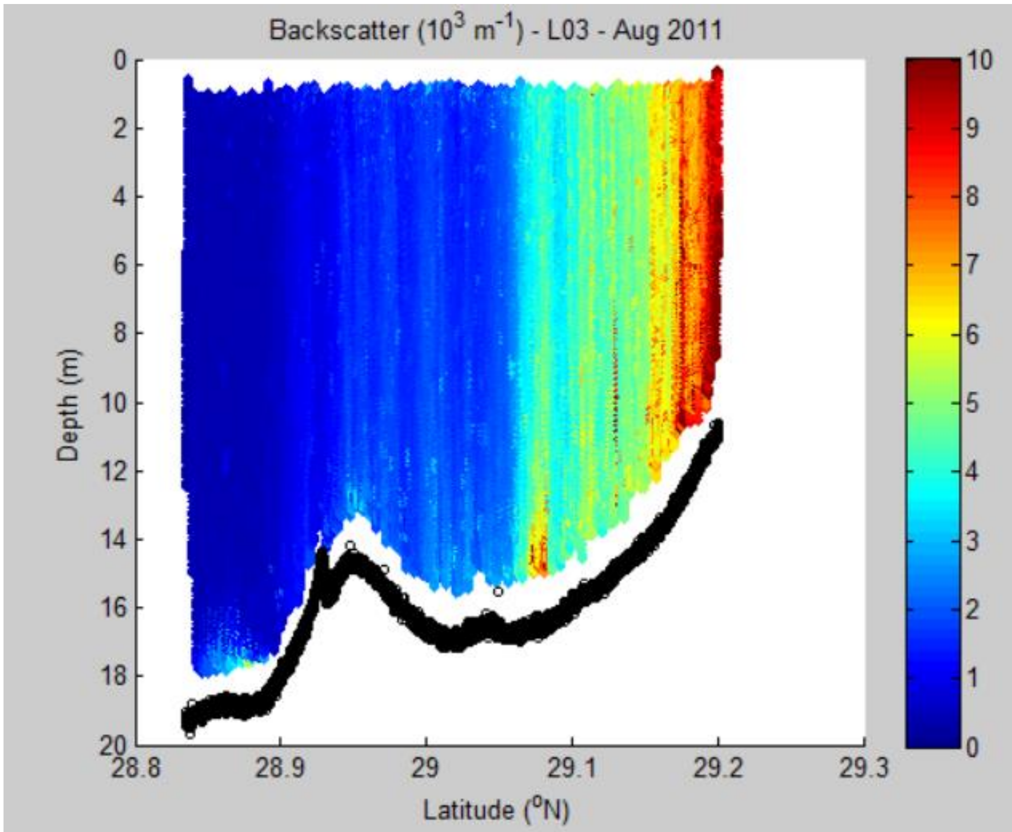


Figure 15: Backscatter from August 2011 Acrobat data along line L03. Uniform backscatter throughout the water column indicates full or near-full water column mixing in shallow water near the coast.

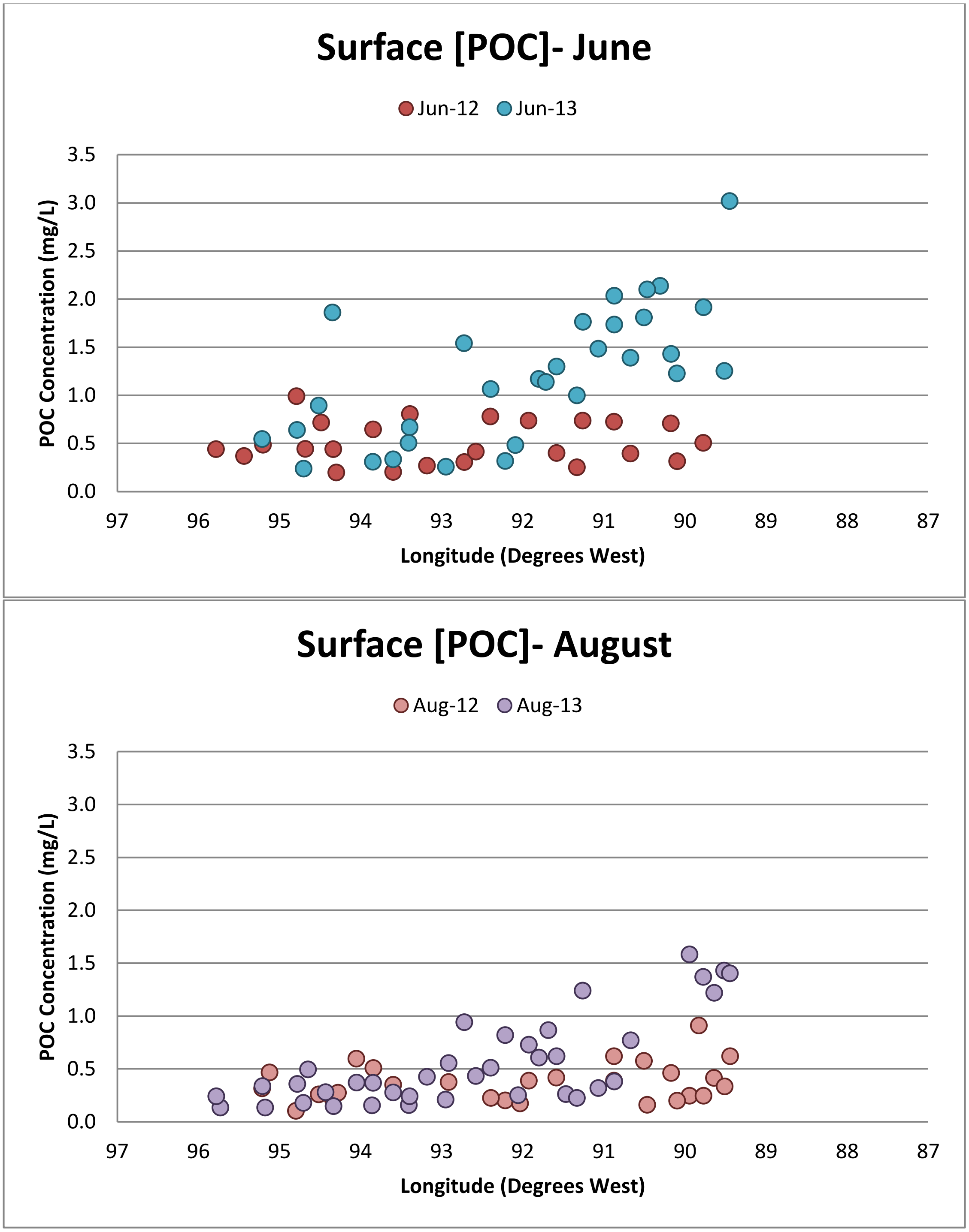
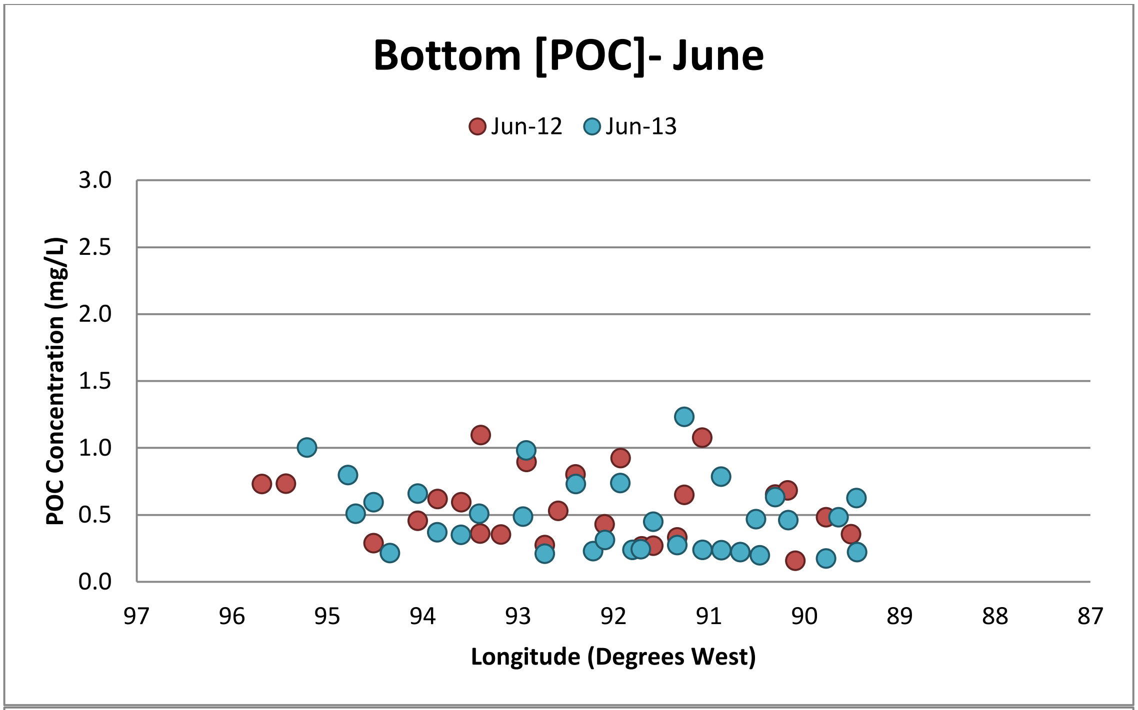


Figure 16: Top panel: surface POC concentrations for statistically different conditions: flood conditions (June 2013) vs. drought conditions (June 2012). Bottom panel: surface POC concentrations for conditions that are not statistically different: normal conditions (August 2013) vs. drought conditions (August 2012).



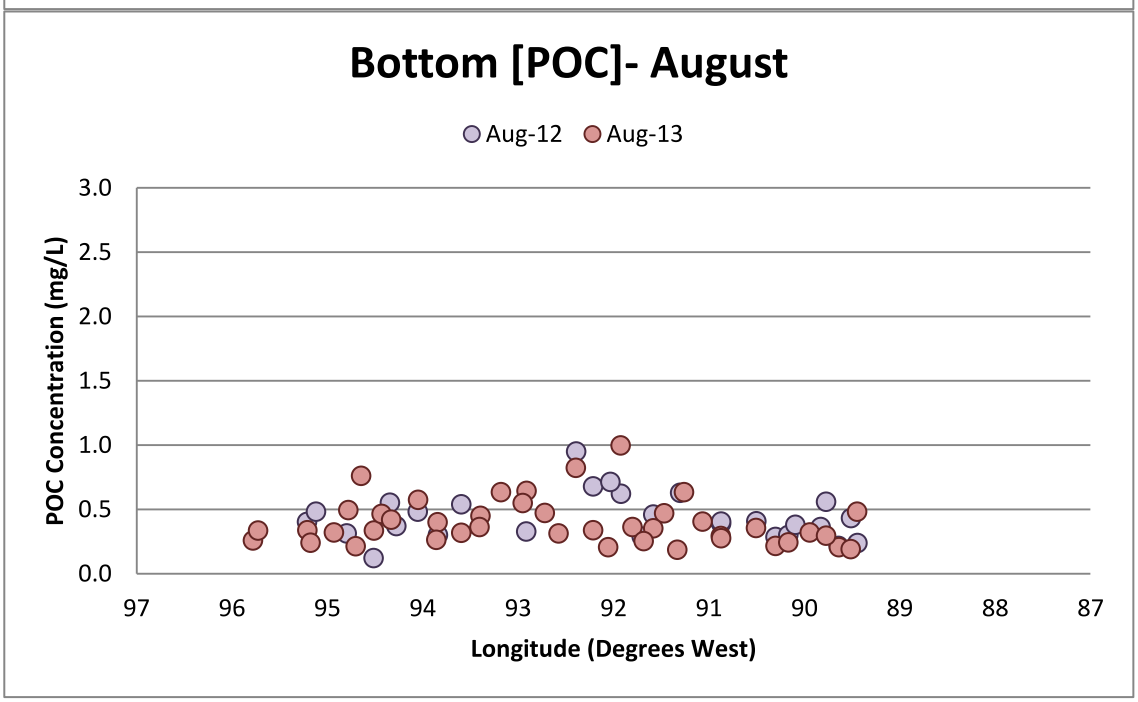
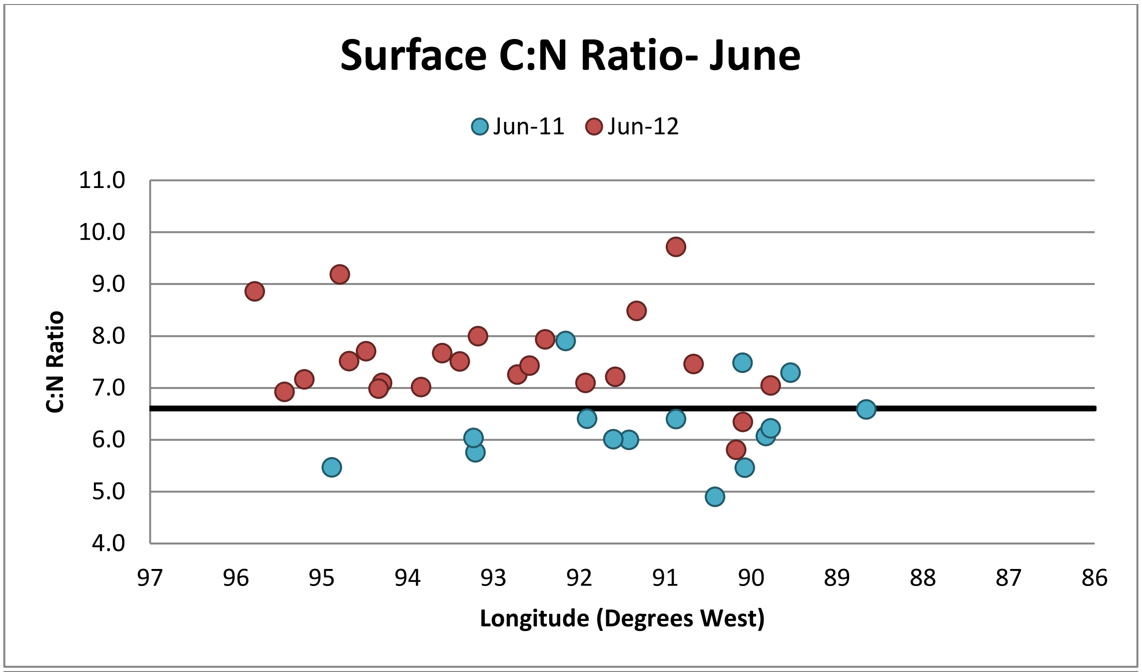


Figure 17: Top panel: bottom PM concentrations for conditions that are not statistically different: flood conditions (June 2013) vs. drought conditions (June 2012).
Bottom panel: bottom PM concentrations for conditions that are not statistically different: normal conditions (August 2013) vs. drought conditions (August 2012).



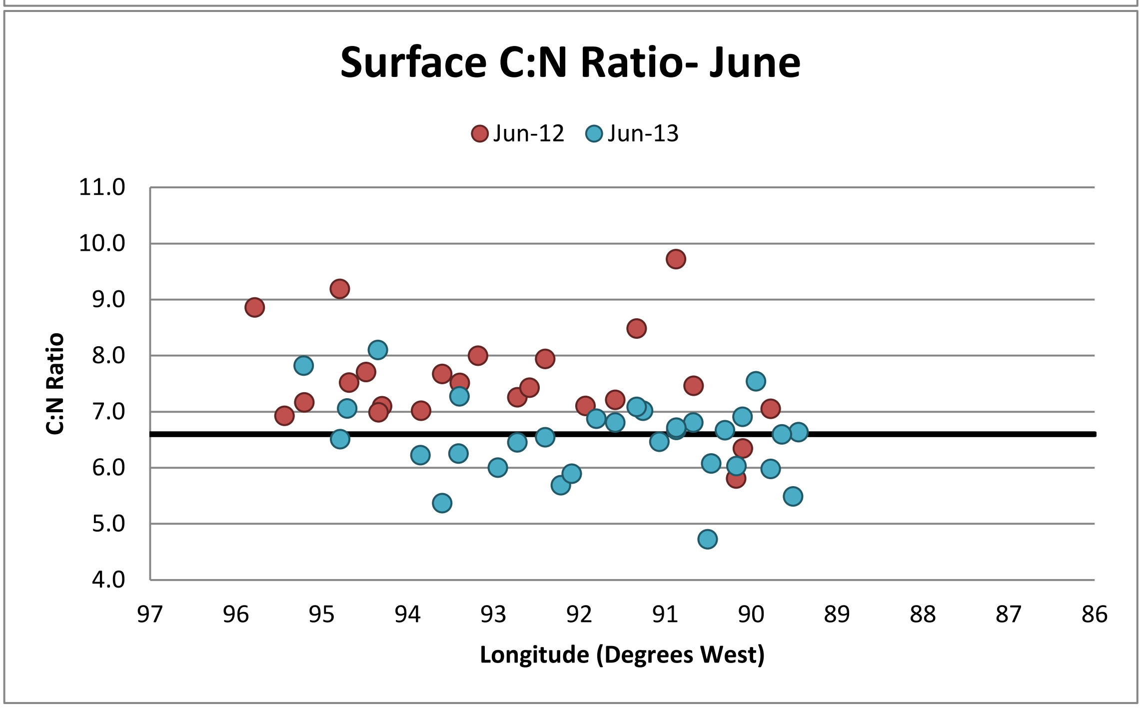


Figure 18: Top panel: surface C:N ratios for statistically different conditions: flood conditions (June 2011) vs. drought conditions (June 2012).
Bottom panel: surface C:N ratios for statistically different: flood conditions (June 2013) vs. drought conditions (June 2012).
The black line at 6.6 is the Redfield ratio for new phytoplankton.

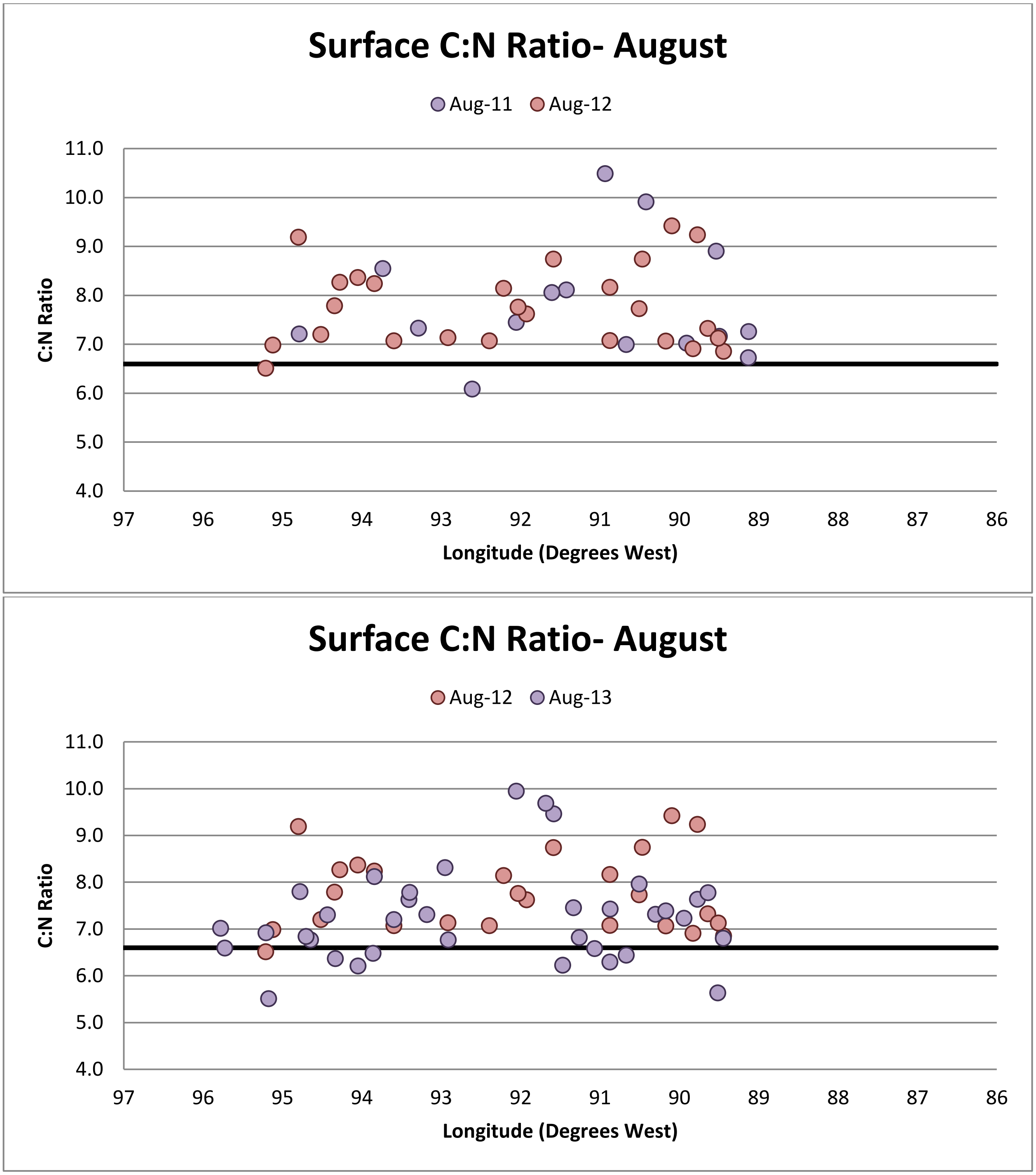


Figure 19: Top panel: surface C:N ratios for conditions that are not statistically different:: normal conditions (August 2011) vs. drought conditions (August 2012). Bottom panel: surface C:N ratios for statistically different: normal conditions (August 2013) vs. drought conditions (August 2012).
The black line at 6.6 is the Redfield ratio for new phytoplankton.

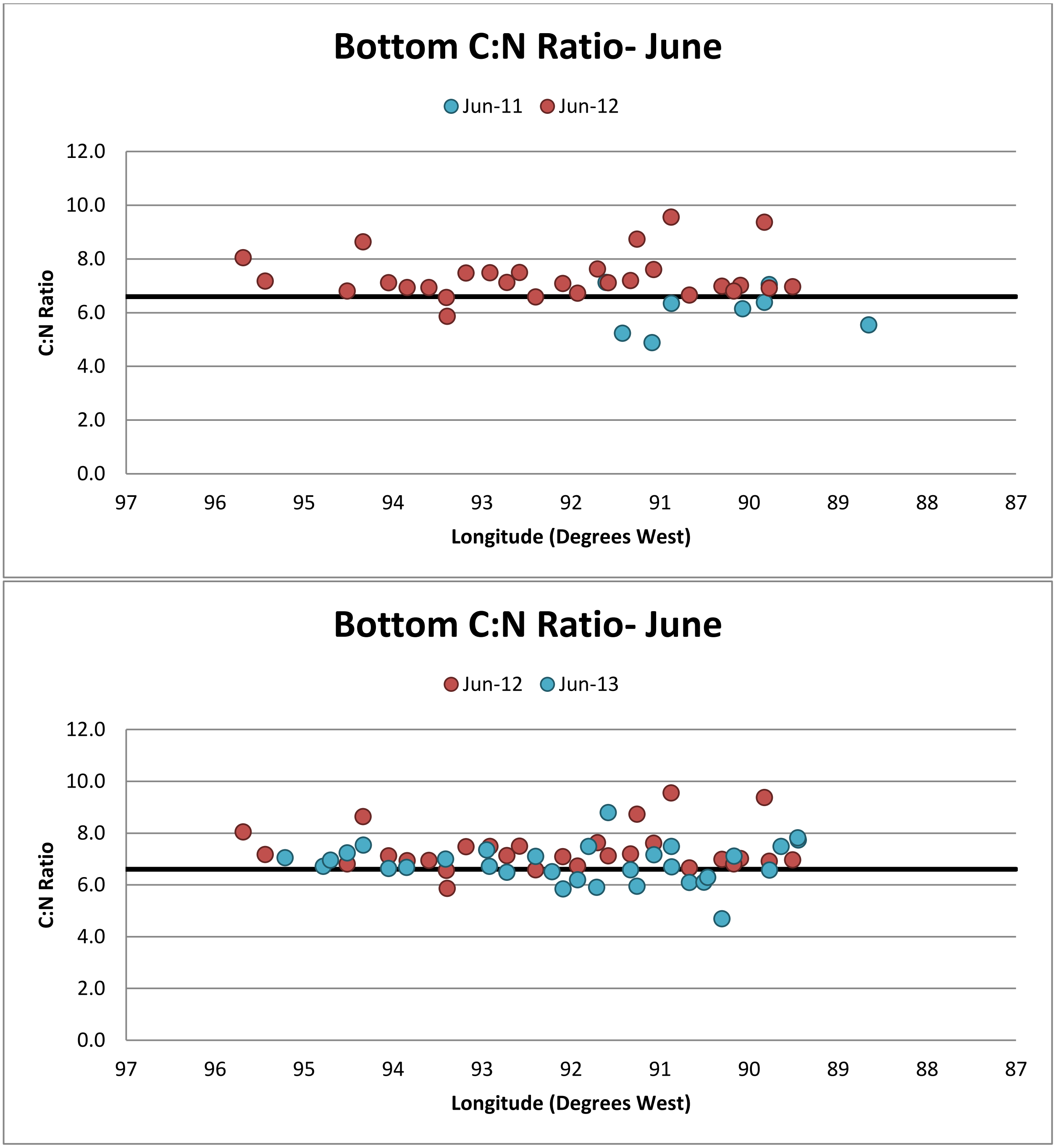
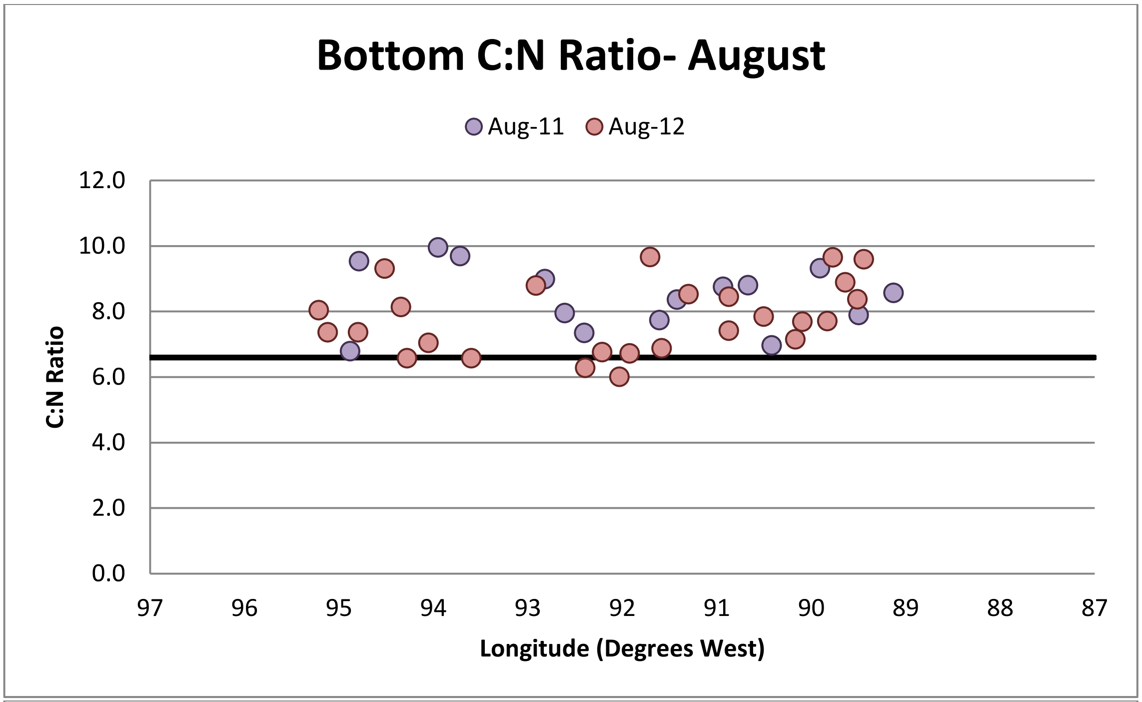


Figure 20: Top panel: bottom C:N ratios for statistically different conditions: flood conditions (June 2011) vs. drought conditions (June 2012).
Bottom panel: bottom C:N ratios for statistically different conditions: flood conditions (June 2013) vs. drought conditions (June 2012).
The black line at 6.6 is the Redfield ratio for new phytoplankton.



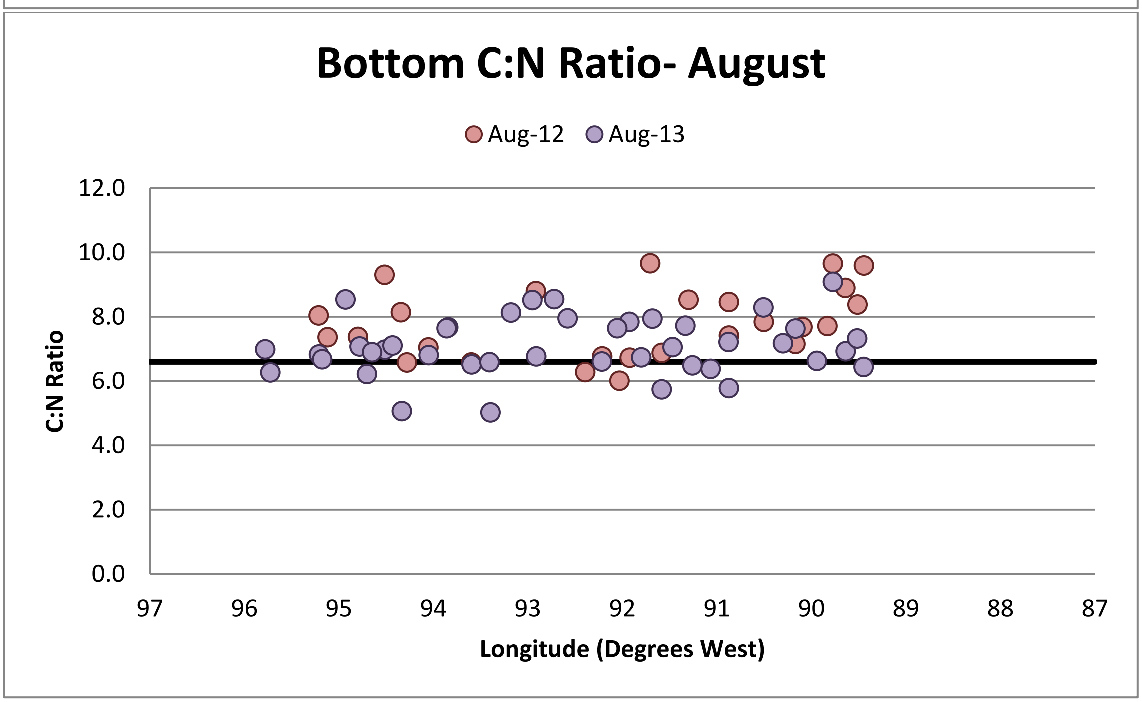


Figure 21: Top panel: bottom C:N ratios for statistically different conditions: normal conditions (August 2011) vs. drought conditions (August 2012). Bottom panel: bottom C:N ratios for conditions that are not statistically different: normal conditions (August 2013) vs. drought conditions (August 2012). The black line at 6.6 is the Redfield ratio for new phytoplankton.

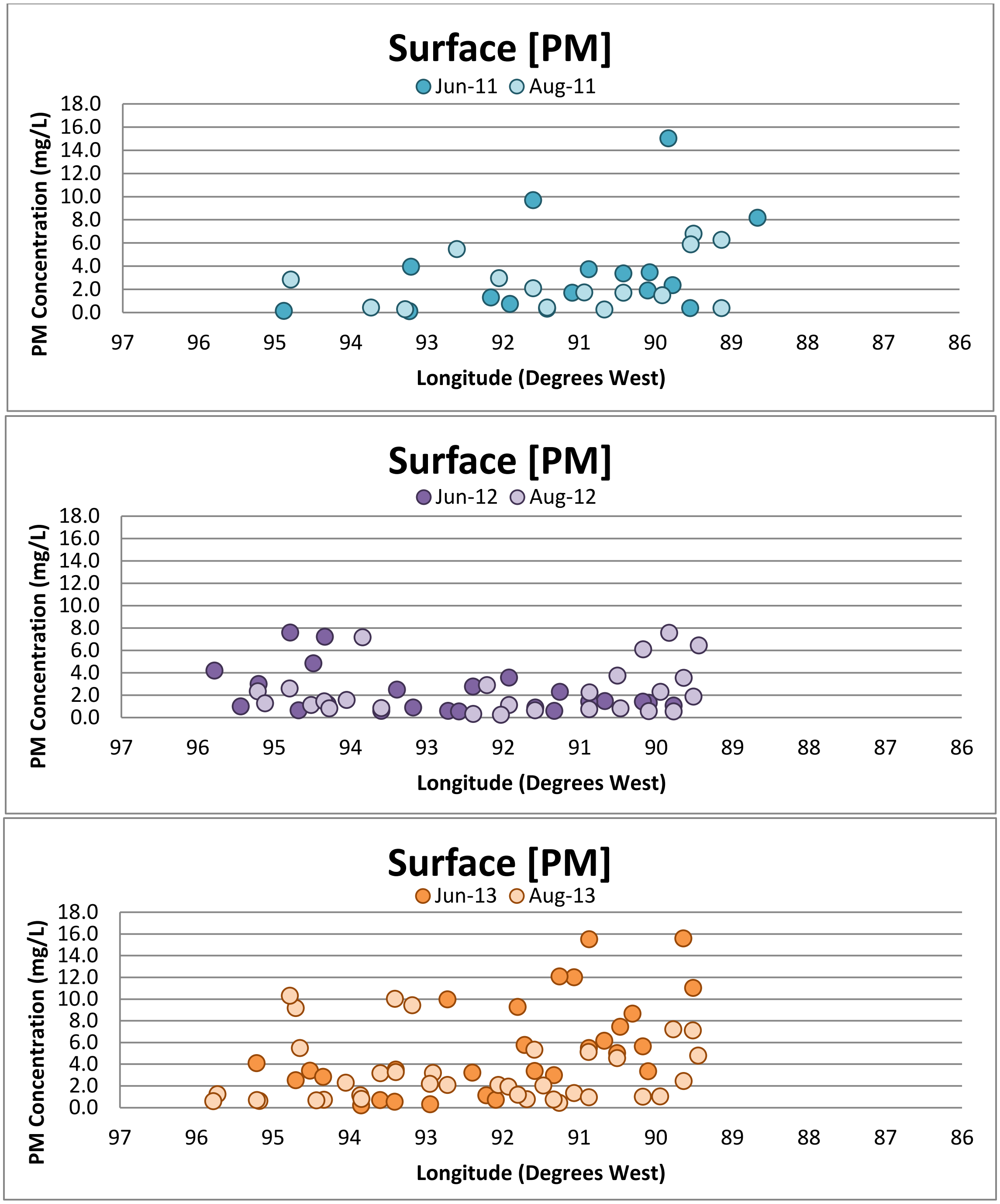


Figure 22: Top panel: surface PM concentrations that are not statistically different in 2011.
Middle panel: surface PM concentrations that are not statistically different in 2012.
Bottom panel: surface PM concentrations that are statistically different in 2013.

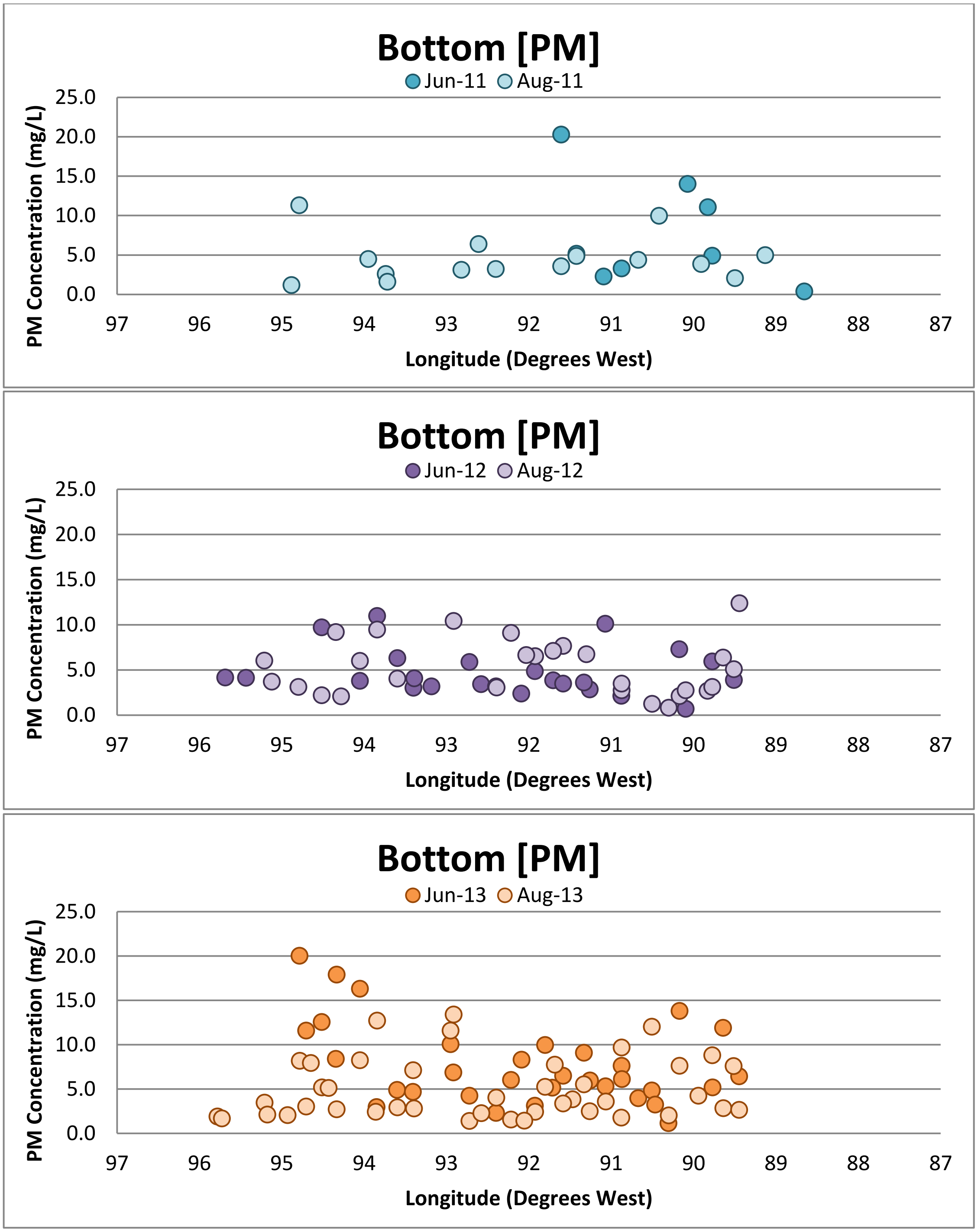


Figure 23: Top panel: bottom PM concentrations that are not statistically different for 2011.
Middle panel: bottom PM concentrations that are not statistically different for 2012.
Bottom panel: bottom PM concentrations that are statistically different for 2013.

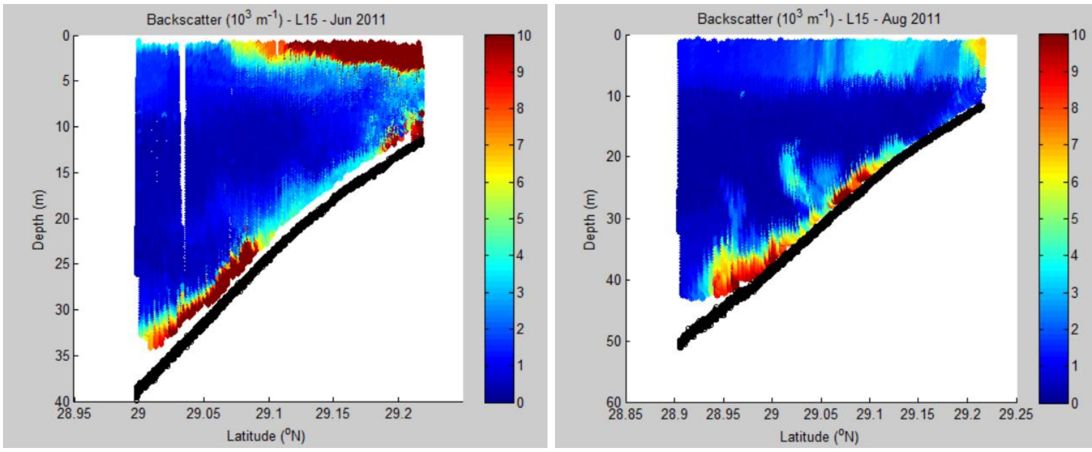


Figure 24: Backscatter in June, 2011 (MS03), and August, 2011 (MS04), along Acrobat line L15 near the Mississippi River (see Figure 3). See text for discussion.

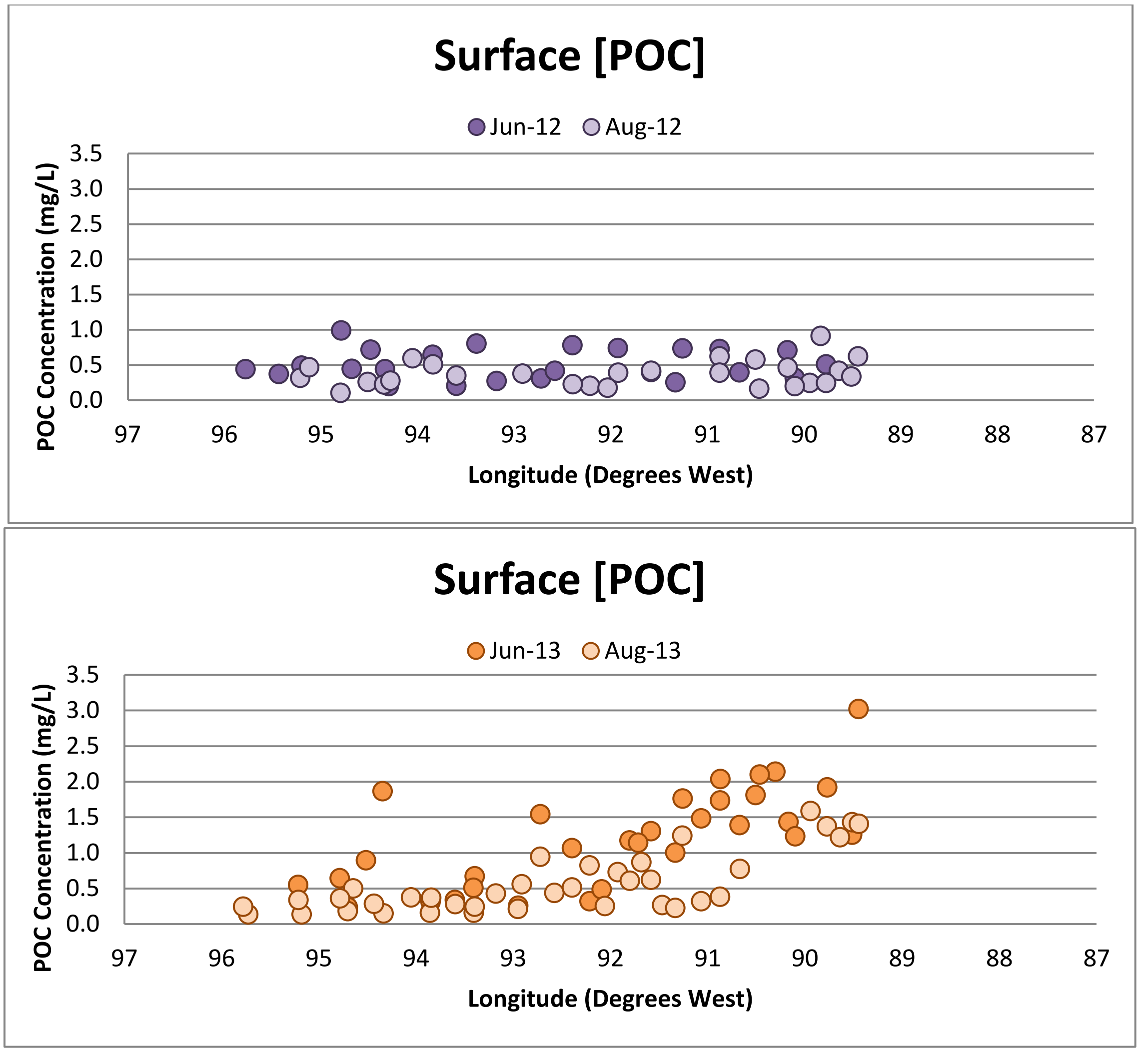


Figure 25: Top panel: surface POC concentrations that are statistically different for 2012.
Bottom panel: surface POC concentrations that are statistically different for 2013.

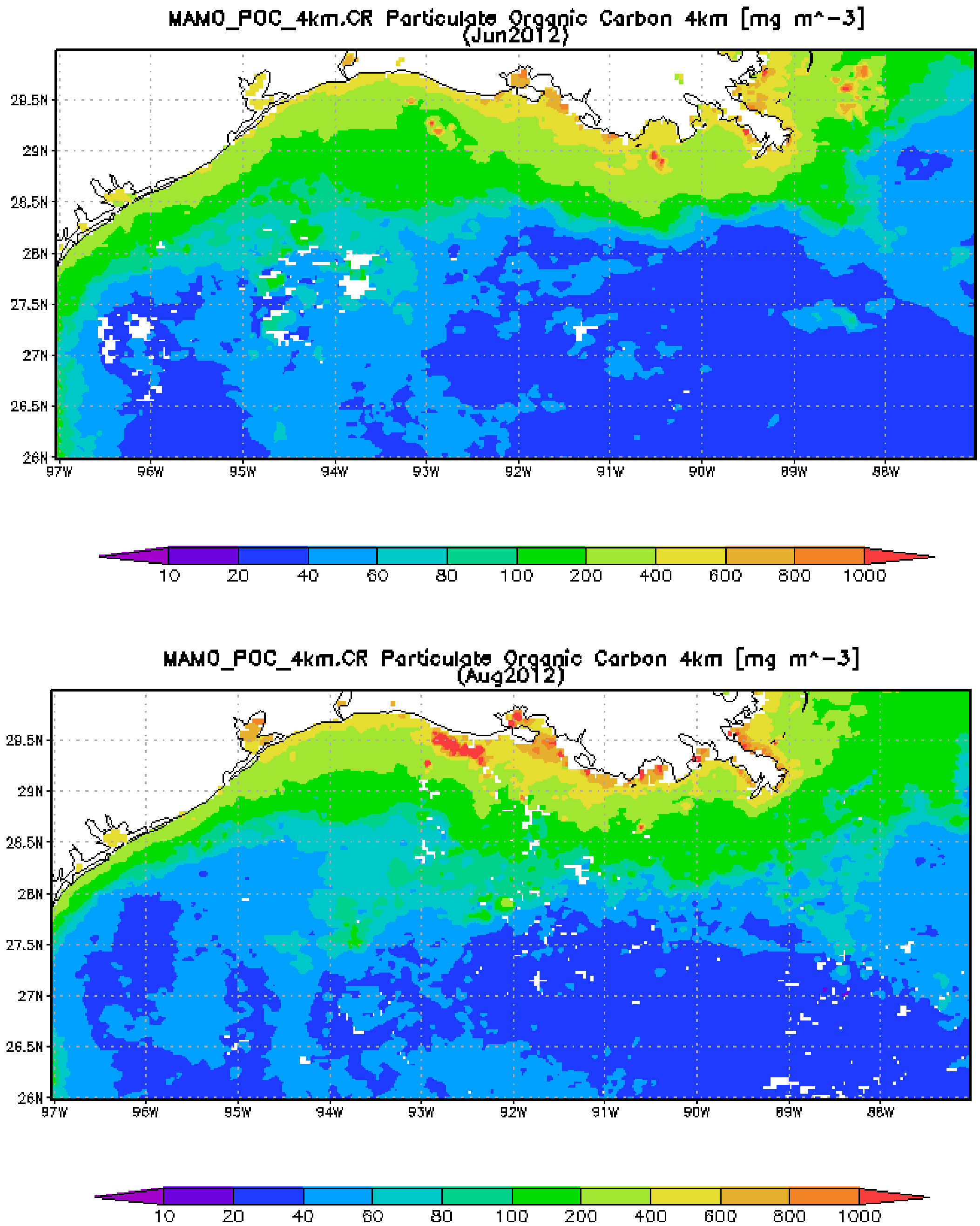


Figure 26: Maps of the northern Gulf of Mexico from satellite data showing near-surface POC concentrations (mg/m^3) for June and August of 2012. Average POC concentration for June of 2012 is 135.358 mg/m^3, and average POC concentration for August of 2012 is 131.714 mg/m^3.

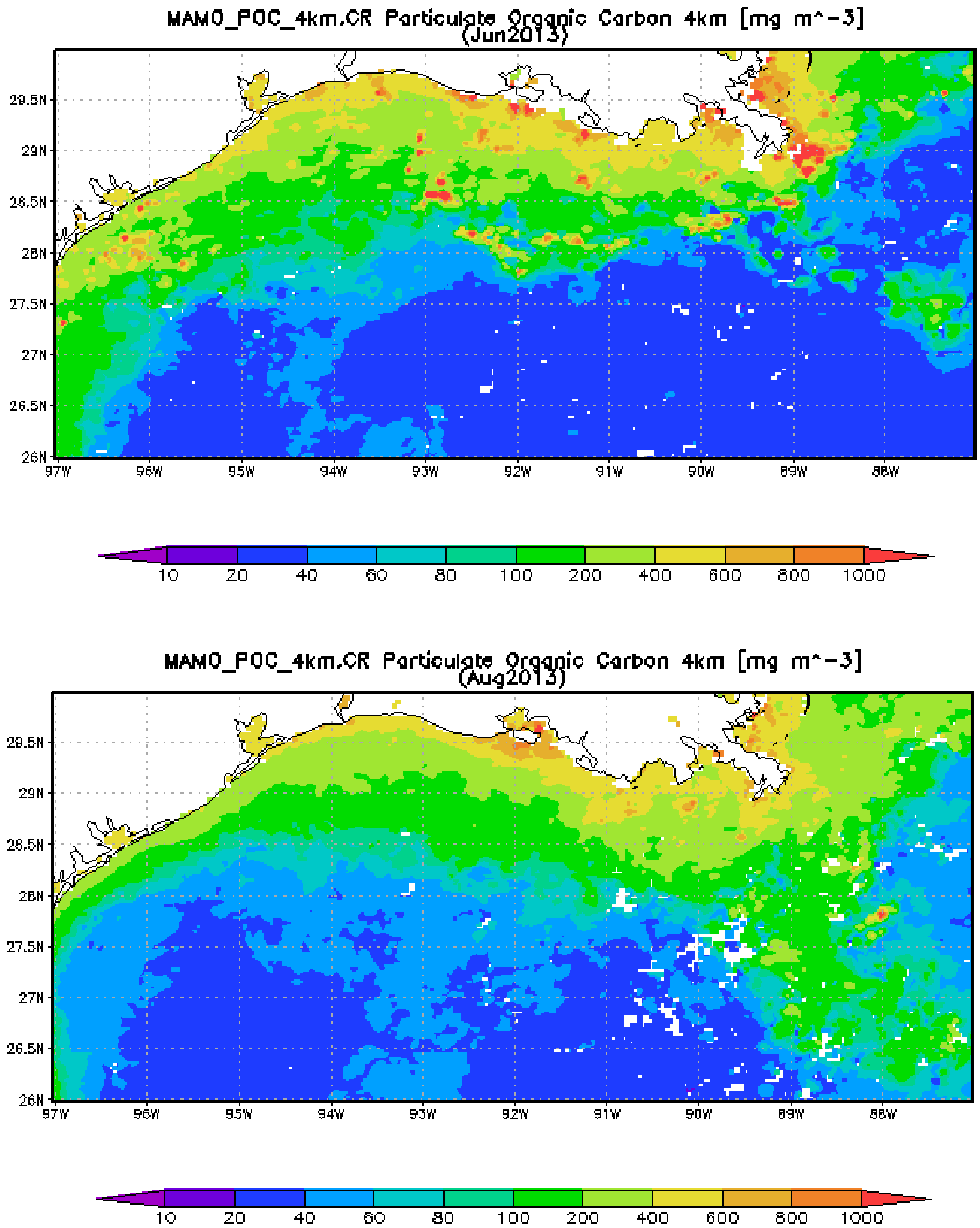


Figure 27: Maps of the northern Gulf of Mexico from satellite data showing near-surface POC concentrations (mg/m^3) for June and August of 2013. Average POC concentration for June of 2013 is 178.773 mg/m^3, and average POC concentration for August of 2013 is 158.465 mg/m^3.

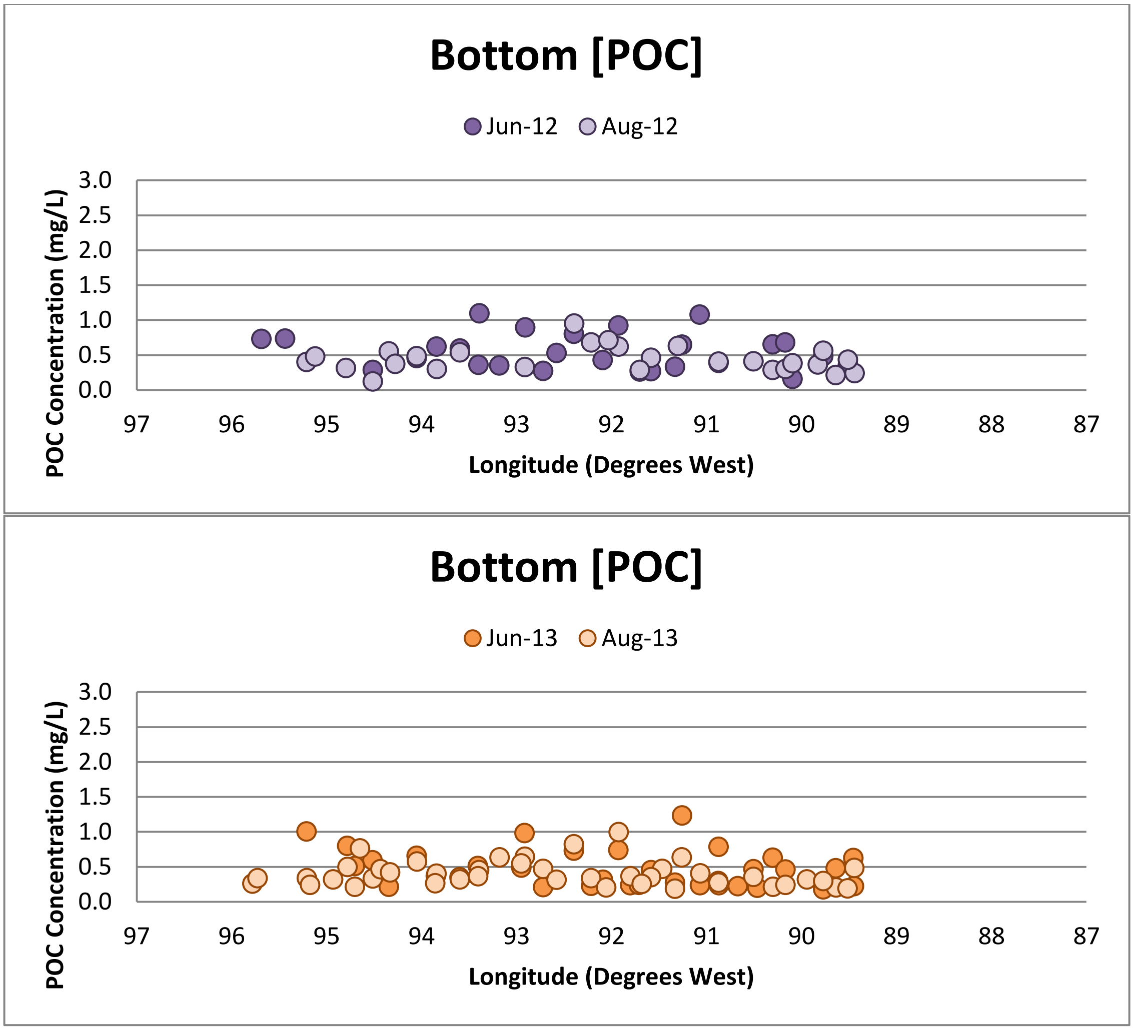


Figure 28: Top panel: bottom POC concentrations that are not statistically different for 2012.
Bottom panel: bottom POC concentrations that are not statistically different for 2013.

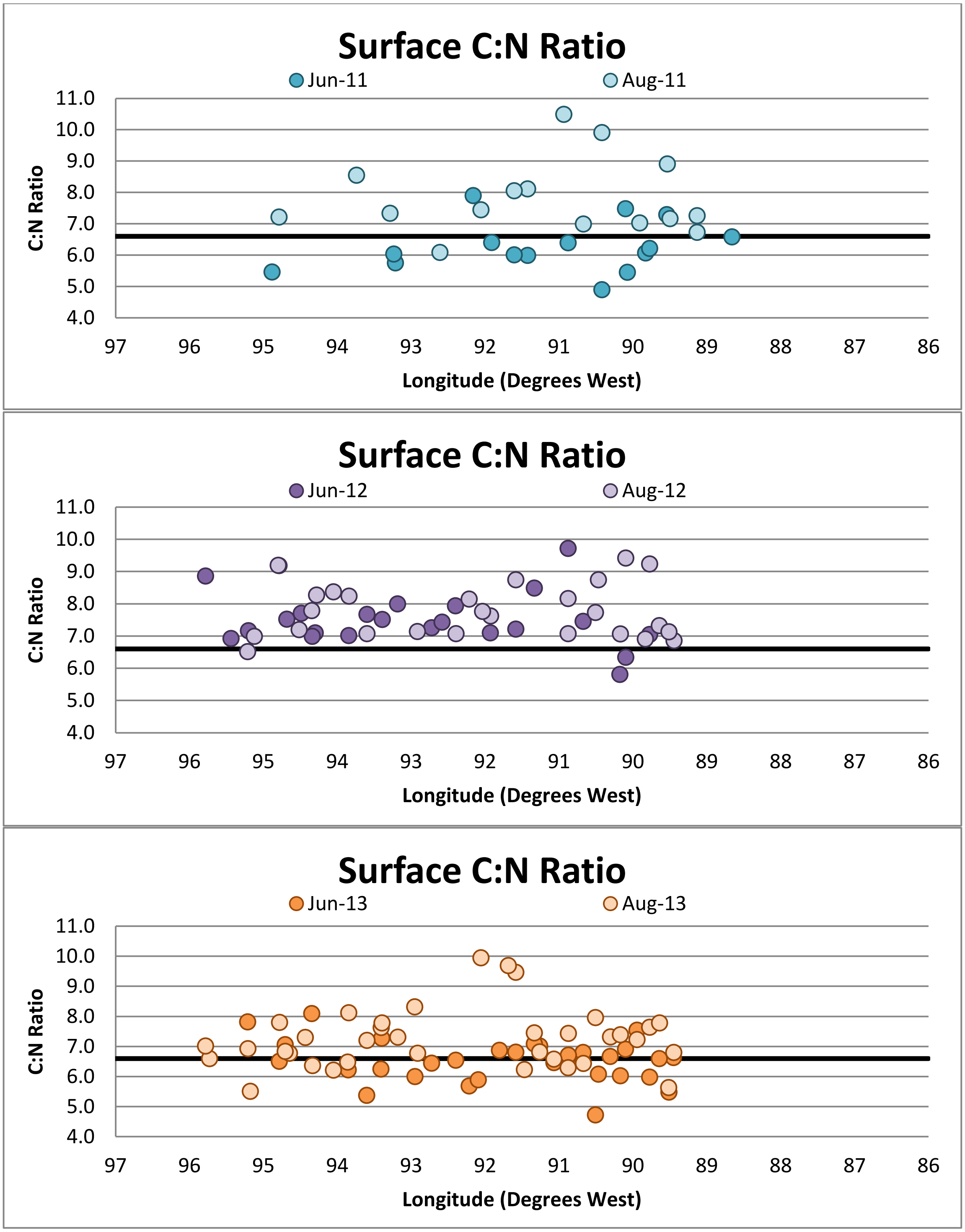


Figure 29:Top panel: surface C:N ratios that are statistically different for 2011. Middle panel: surface C:N ratios that are not stastically different for 2012. Bottom panel: surface C:N ratios that are statistically different for 2013.

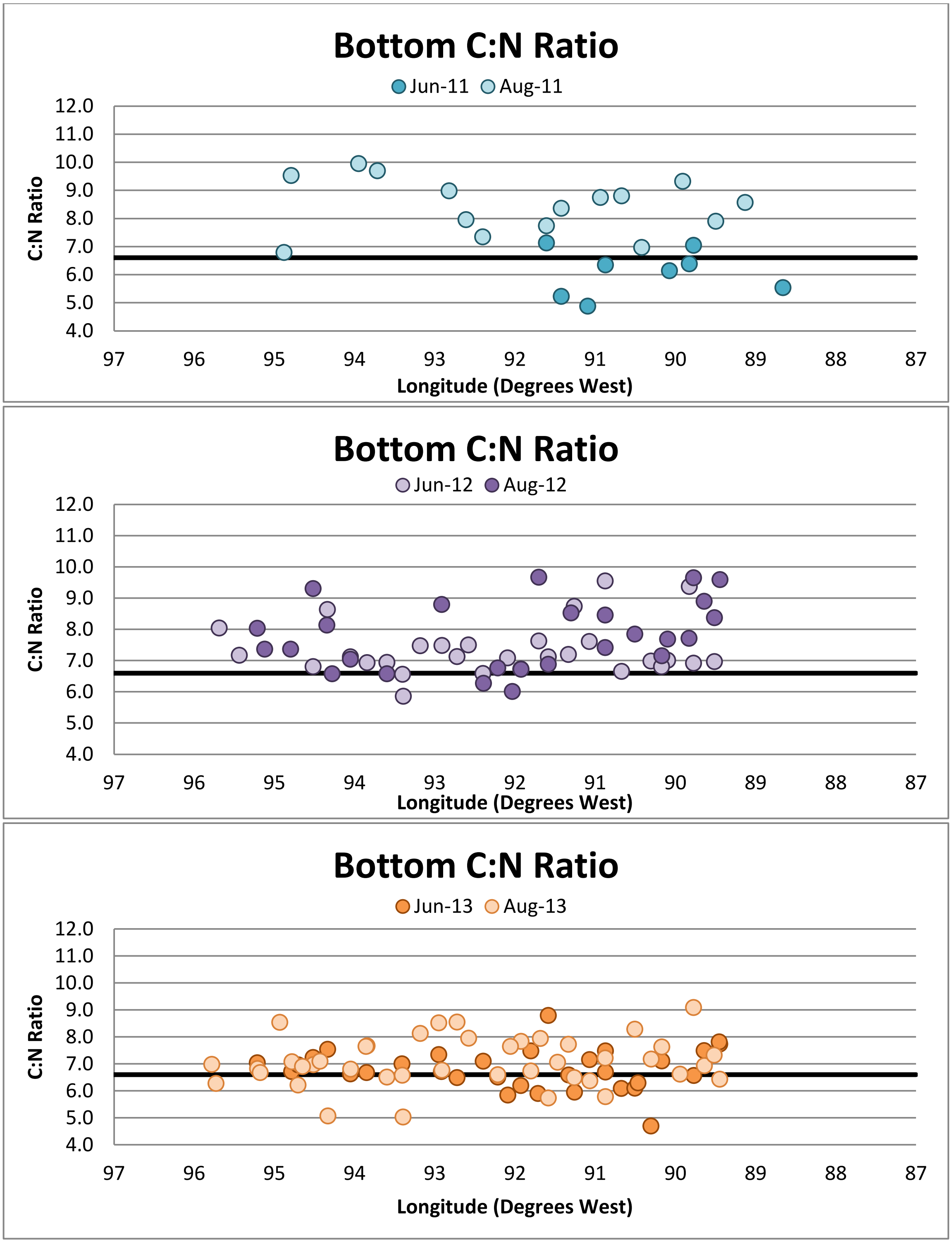


Figure 30: Top panel: bottom C:N ratios that are statistically different for 2011. Middle panel: bottom C:N ratios that are not statistically different for 2012. Bottom panel: bottom C:N ratios that are statistically different for 2013.

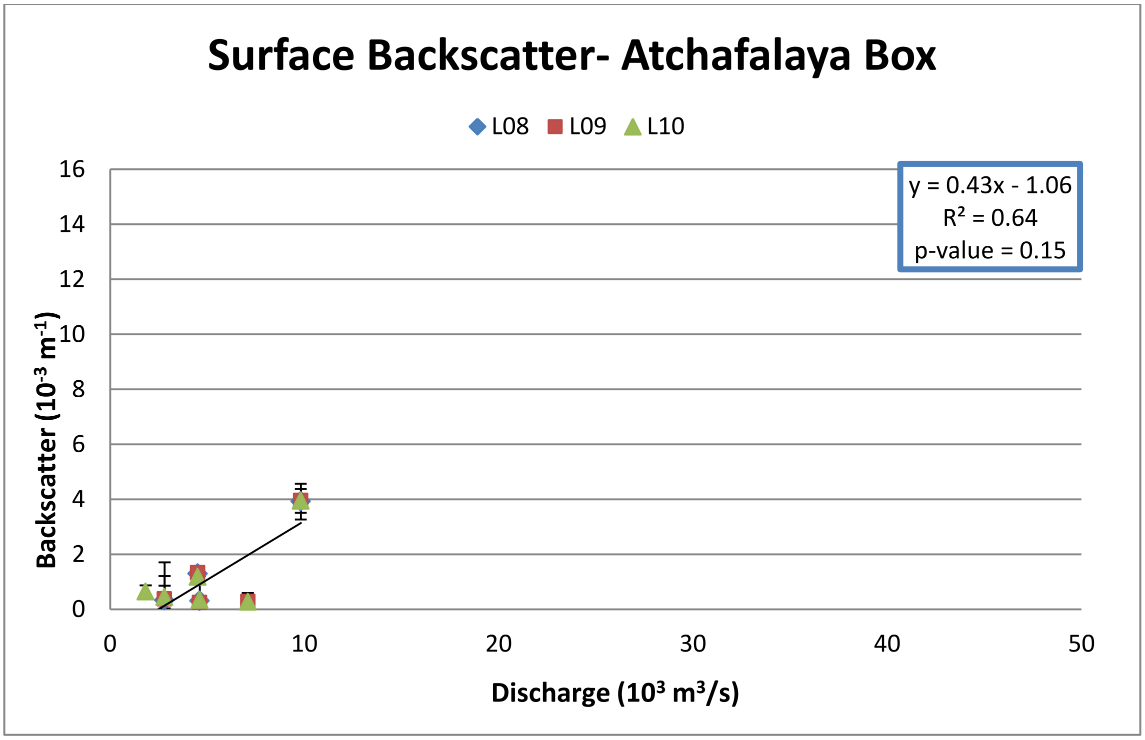


Figure 31: Surface mean backscatter values from Acrobat lines L08, L09, and L10 verses Atchafalaya River discharge for the Atchafalaya Box. The linear regression includes data from the six cruises in 2011-2014.

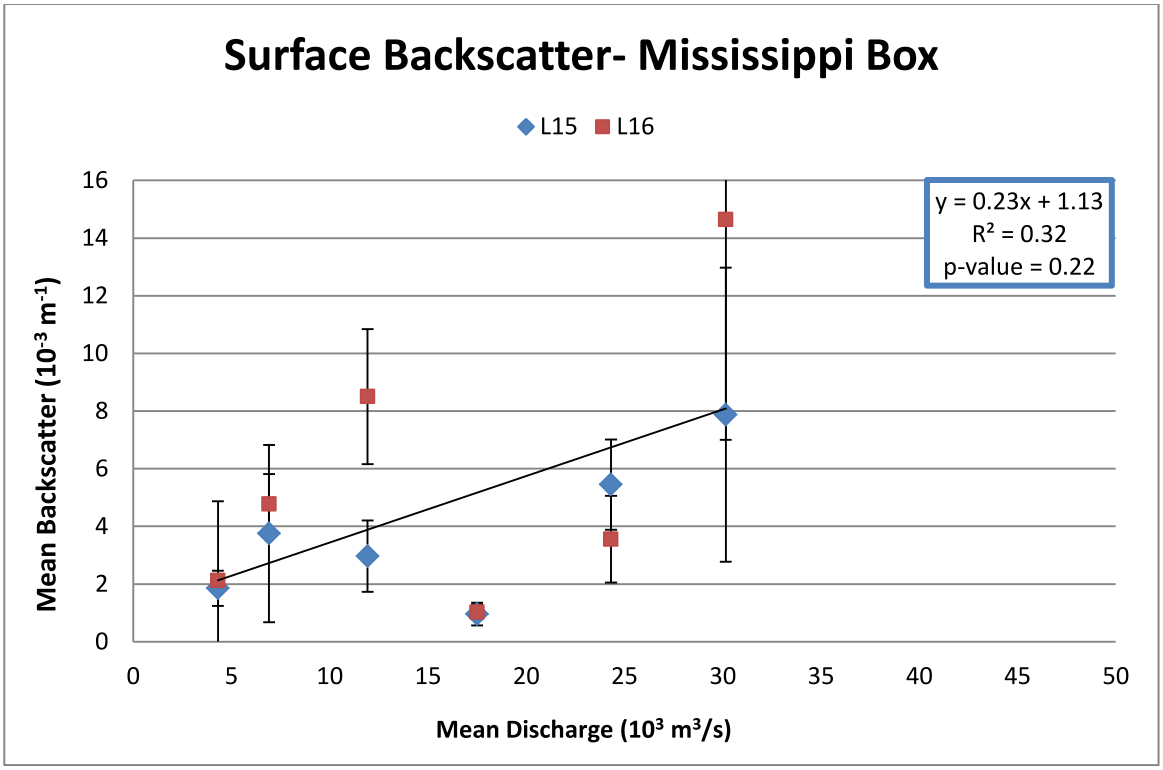


Figure 32: Surface mean backscatter values from Acrobat line L15 and L16 verses Mississippi River discharge for the Mississippi Box. The linear regression includes data from the six cruises in 2011-2014.

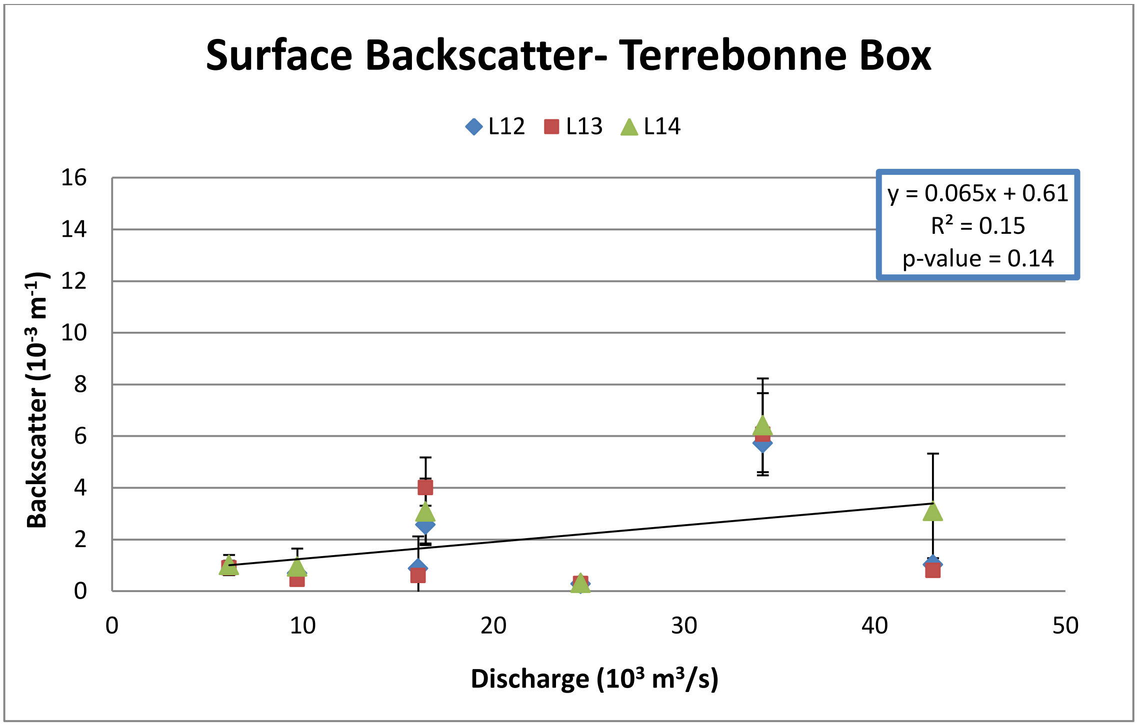
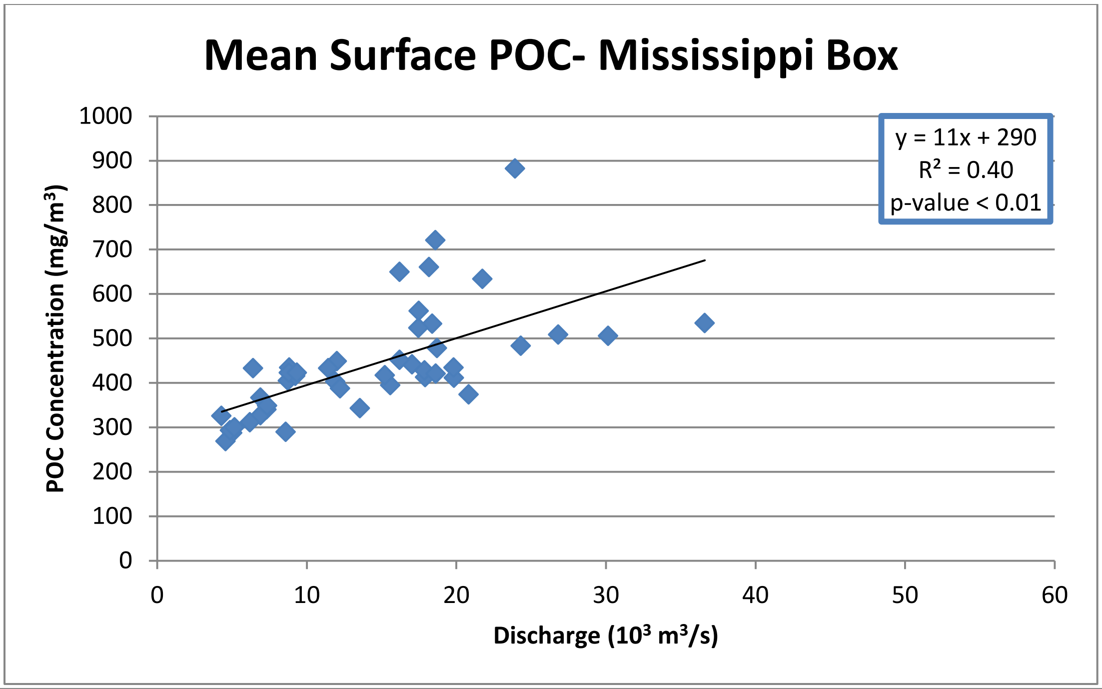


Figure 33: Surface mean backscatter values from Acrobat lines L12, L13, and L14 verses combined Mississippi and Atchafalaya River discharge for the Terrebonne Box. The linear regression includes data from the six cruises in 2011-2014.



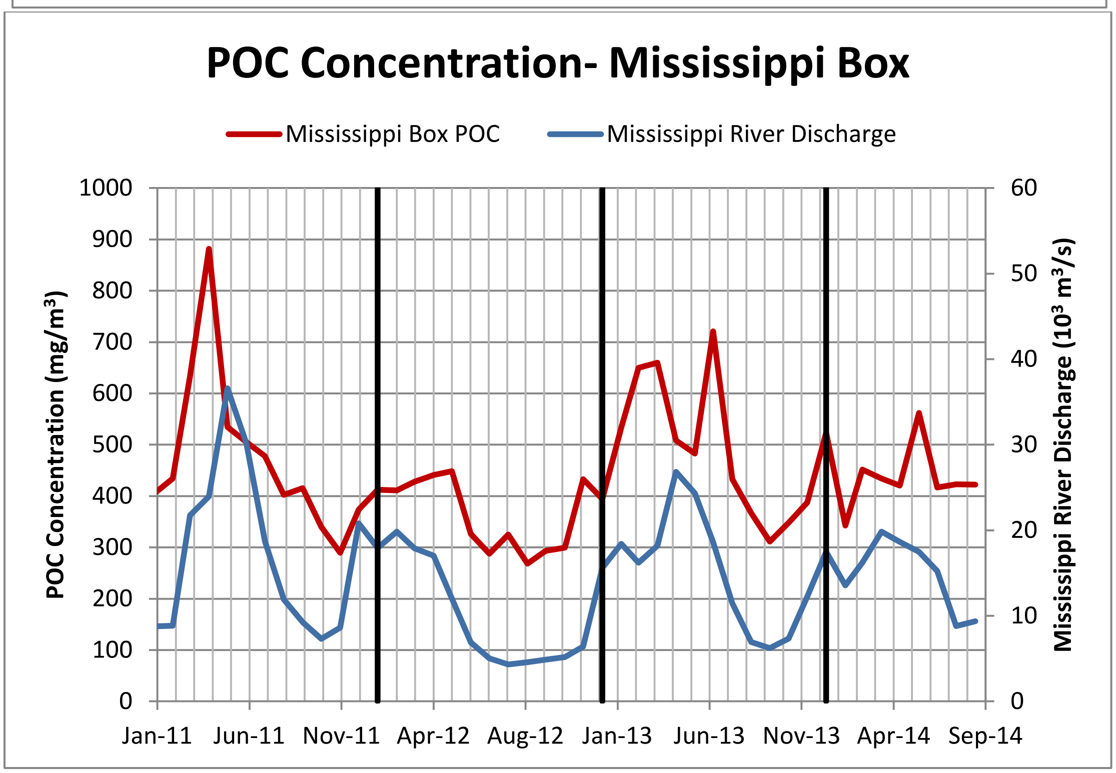
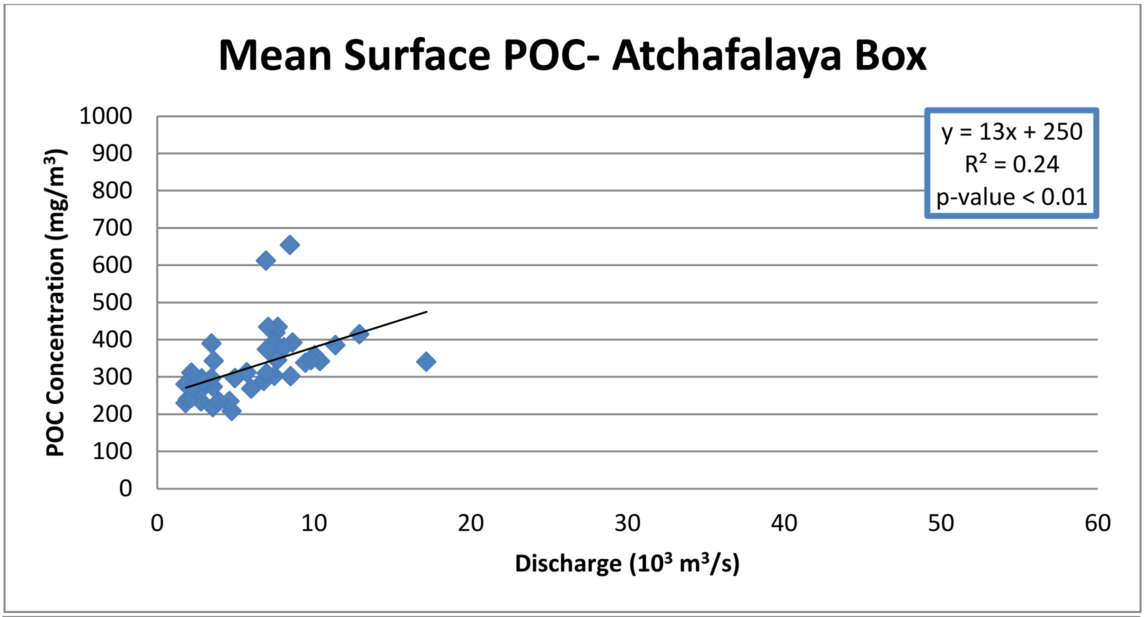


Figure 34: Monthly mean POC concentrations from satellite data in the Mississippi Box and monthly mean river discharge of the Mississippi River shown as a scatter plot (upper) and time series (lower) from January 2011 to September 2014. Black vertical lines represent January 1st.



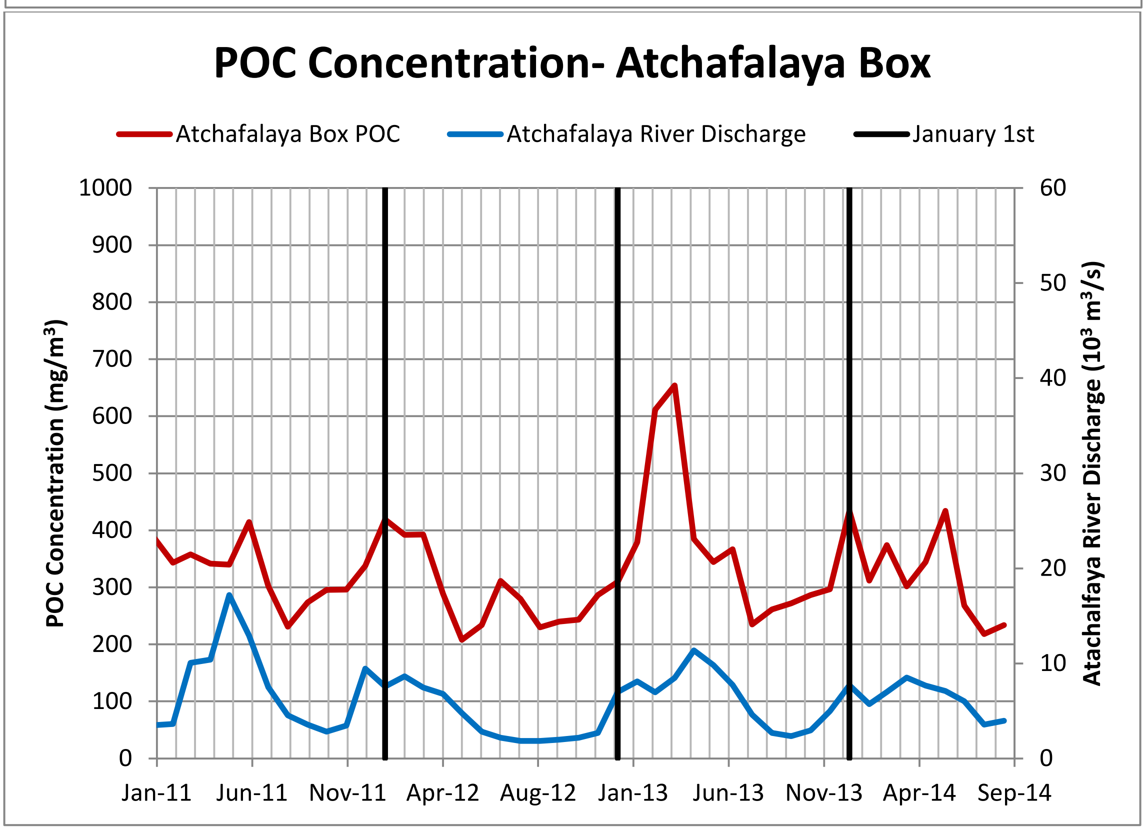


Figure 35: Monthly mean POC concentrations from satellite data in the Atchafalaya Box and monthly mean river discharge of the Atchafalaya River shown as a scatter plot (upper) and time series (lower) from January 2011 to September 2014. Black vertical lines represent January 1st.

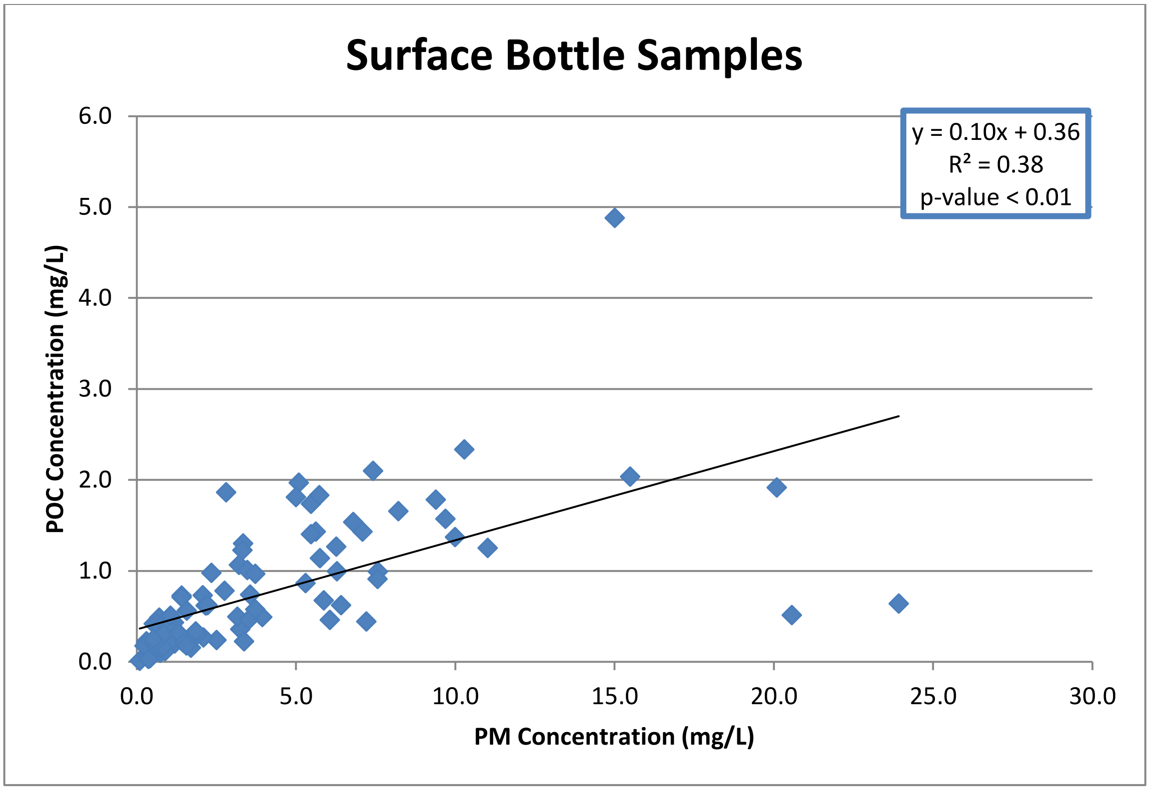
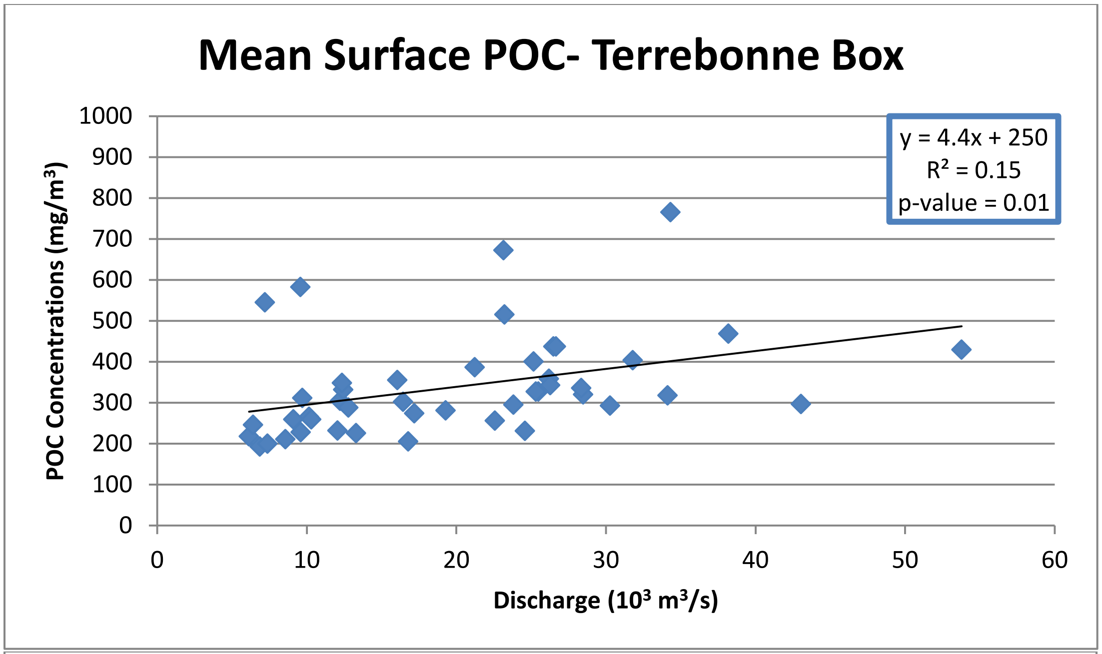


Figure 36: Surface bottle data for POC concentrations and PM concentrations from all CTD casts in the study area.



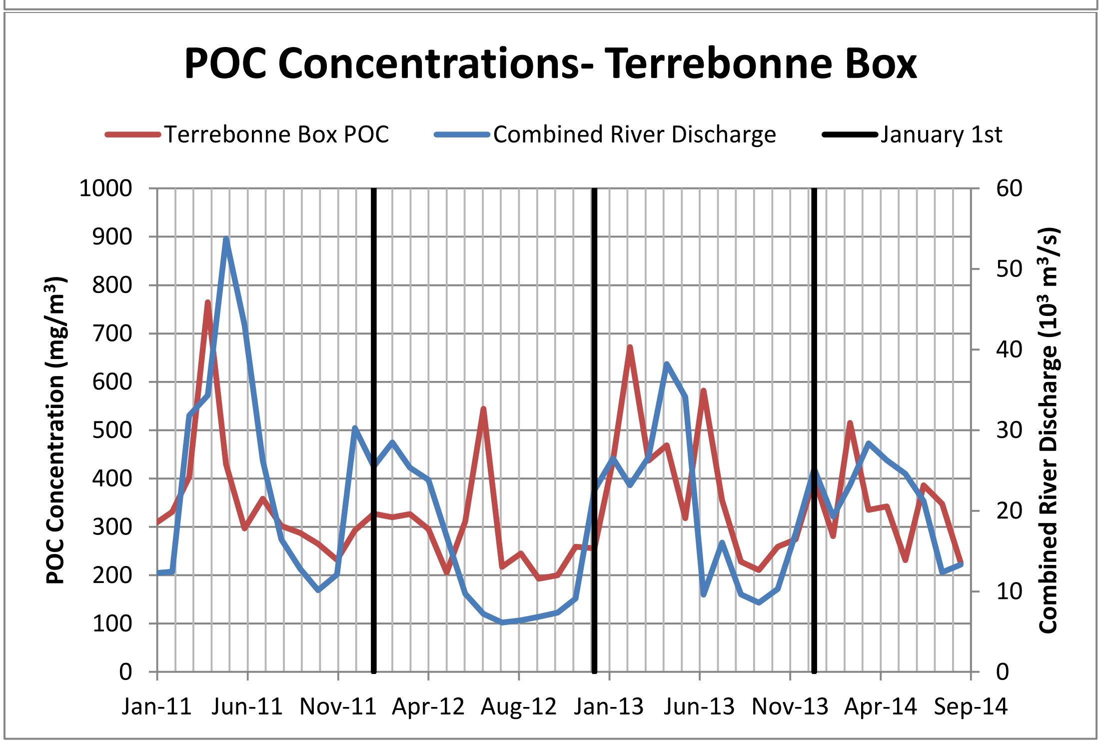
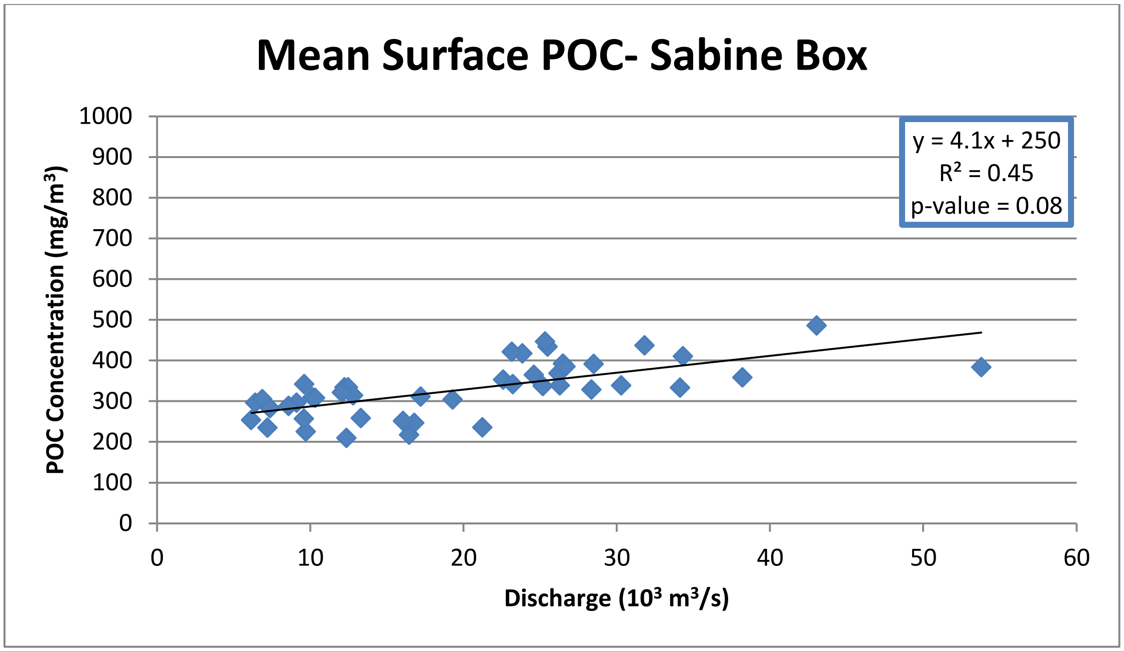


Figure 37: Monthly mean POC concentrations from satellite data in the Terrebonne Box and monthly mean river discharge of the combined Mississippi and Atchafalaya Rivers shown as a scatter plot (upper) and time series (lower) from January 2011 to September 2014. Black vertical lines represent January 1st.



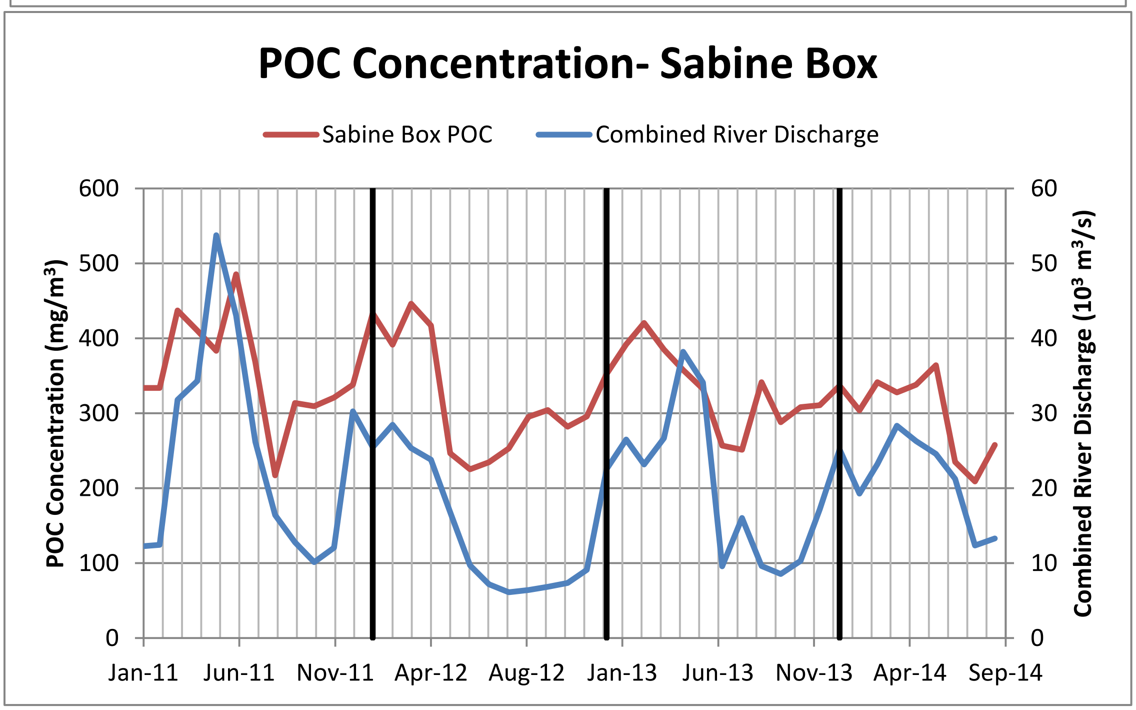


Figure 38: Monthly mean POC concentrations from satellite data in the Sabine Box and monthly mean river discharge of the combined Mississippi and Atchafalaya Rivers shown as a scatter plot (upper) and time series (lower) from January 2011 to September 2014. Black vertical lines represent January 1st.

APPENDIX B

TABLES

Cruise Name	Cruise Start Date	Cruise End Date	Deviation from Climatology	River Discharge (m^3/s)
MS03	June 23, 2011	July 1, 2011	Flood	30,158
MS04	August 7, 2011	August 15, 2011	Normal	11,928
MS05	June 11, 2012	June 16, 2012	Drought	6,913
MS06	August 14, 2012	August 21, 2012	Drought	4,313
MS07	June 18, 2013	June 25, 2013	Flood	24,313
MS08	August 3, 2013	August 10, 2013	Normal	11,446
MS09	June 17, 2014	June 23, 2014	Normal	17,500

Table 1: Start and end dates for all cruises studied and river discharge deviation from climatology based on Figure 2. River conditions are based on the US Drought Monitor System's classification using the 80th (flood conditions, discharge above 20,172 m^3/s) and 20th (drought conditions, discharge below 8,598 m^3/s) percentiles of the 10 year average. River Discharge is from the Mississippi River (Gauging Station USGS 07374000) and is a monthly average for each cruise's departure month (USGS, 2015).

Shipboard Flow-Through	CTD	Acrobat
Near surface measurements	Measurements at nominal top, middle, and bottom depths	Measurements from 1m below the surface to 1m above the seafloor
Beam c_p WetLabs Transmissometer PM Proxy	Backscatter: 700 nm WetLabs FLNTU[1] (deep) PM Proxy	Backscatter: 700nm WetLabs FLNTU (shallow) PM Proxy
Chlorophyll *a* fluorescence Chelsea Aquatracker III (MS07 Only)	Chlorophyll *a* fluorescence WetLabs FLNTU (deep) 470/695 nm	Chlorophyll *a* fluorescence WetLabs FLNTU (shallow) 470/695 nm
CDOM Fluorescence WetLabs FLCD[2] 370/460nm		CDOM fluorescence WetLabs FLCD 370/460 nm
Salinity	Salinity	Salinity
Temperature	Temperature	Temperature
	Dissolved O_2	Dissolved O_2
	PAR	

Table 2: Shipboard instruments used to collect data for MS03-MS08.
[1] FLNTU: Chlorophyll *a* fluorometer with a back scattering measurement at 700nm for simultaneous determination of turbidity
[2]FLCD: Fluorometer measuring colored dissolved organic matter (CDOM).

Area	West	North	South	East
Northern Gulf of Mexico (NGOM) Box	-97.0	30.0	27.0	-88.0
Sabine Box	-93.8	29.5	29.1	-93.3
Atchafalaya Box	-92.7	29.3	28.7	-91.7
Terrebonne Box	-91.0	29.0	28.5	-90.0
Mississippi Box	-90.0	29.2	28.8	-89.3
Mid- Shelf Box	-92.0	28.5	28.2	-91.0

Table 3: Latitude and Longitude for each of the six boxes analyzed. Data from these boxes are used for averaging surface POC concentrations from satellite data and surface and bottom PM concentrations from Acrobat data.

Cruise	Nominal Depth	Slope	Intercept	R^2
MS03	Top	0.83	-3.5	0.81
MS03	Bottom	0.52	1.1	0.61
MS04	Top	0.70	1.6	0.60
MS04	Bottom	1.01	-4.1	0.98
MS05	Top	0.63	-1.9	0.35
MS05	Bottom	0.61	-0.5	0.53
MS06	Top	0.70	-1.8	0.40
MS06	Bottom	0.80	-2.3	0.88
MS07	Top	0.70	4.3	0.36
MS07	Bottom	0.96	0.4	0.86
MS08	Top	0.35	3.2	0.09
MS08	Bottom	0.81	1.7	0.54
MS09	Top	0.22	0.6	0.36
MS09	Bottom	0.30	0.9	0.31

Table 4: Slope, intercept, and R^2 values for the surface and bottom bottle PM concentrations vs Acrobat backscatter, b_b, for all cruises in the study. Backscatter values are used as a proxy for PM concentration.

A vs B	Cruises	Variable	Alt. Hypothesis	P-Value	Decision
Flood v Drought	Jun ’11 v Jun ‘12	PM	A>B	.5250	Do not reject
Flood v Drought	Jun ‘13 v Jun ‘12	PM	A>B	.0021	Reject
Flood v Normal	Jun ’11 v Jun ‘14	PM	A>B	.1949	Do not reject
Flood v Normal	Jun ’13 v Jun ‘14	PM	A>B	.0006	Reject
Flood v Flood	Jun ’11 v Jun ‘13	PM	A≠B	.0814	Do not reject
Normal v Drought	Jun ’14 v Jun ‘12	PM	A>B	.1691	Do not reject
Normal v Drought	Aug ’11 v Aug ‘12	PM	A>B	.9784	Do not reject
Normal v Drought	Aug ’13 v Aug ‘12	PM	A>B	.3633	Do not reject
Flood v Drought	Jun ’13 v Jun ‘12	POC	A>B	.0001	Reject
Normal v Drought	Aug ’13 v Aug ‘12	POC	A>B	.2495	Do not reject
Flood v Drought	Jun ’11 v Jun ‘12	C:N	B>A	.0003	Reject
Flood v Drought	Jun ’13 v Jun ‘12	C:N	B>A	.0001	Reject
Normal v Drought	Aug ’11 v Aug ‘12	C:N	B>A	.9676	Do not reject
Normal v Drought	Aug ’13 v Aug ‘12	C:N	B>A	.0220	Reject

Table 5: Wilcoxon Rank Sum test results for the surface PM and POC concentrations and C:N based on bottle sample measurements. “Reject” indicates that the null hypothesis is to be rejected and the alternative hypothesis is confirmed. For these tests, POC concentrations for June and August of 2011 and June of 2014 will not be considered, as well as C:N ratios from June 2014, due to differing processing of POC concentrations.

A vs B	Cruises	Variable	Alt. Hypothesis	P-Value	Decision
Flood v Drought	Jun ’11 v Jun ‘12	PM	A>B	.5150	Do not reject
Flood v Drought	Jun ’13 v Jun ‘12	PM	A>B	.0094	Reject
Flood v Normal	Jun ’11 v Jun ‘14	PM	A>B	.4463	Do not reject
Flood v Normal	Jun ’13 v Jun ‘14	PM	A>B	.0019	Reject
Normal v Drought	Jun ’14 v Jun ‘12	PM	A>B	.3628	Do not reject
Normal v Drought	Aug ’11 v Aug ‘12	PM	A>B	.4995	Do not reject
Normal v Drought	Aug ’13 v Aug ‘12	PM	A>B	.5370	Do not reject
Flood v Drought	Jun ’13 v Jun ‘12	POC	A>B	.2468	Do not reject
Normal v Drought	Aug ’13 v Aug ‘12	POC	A>B	.2059	Do not reject
Flood v Drought	Jun ’11 v Jun ‘12	C:N	B>A	.0023	Reject
Flood v Drought	Jun ’13 v Jun ‘12	C:N	B>A	.0105	Reject
Normal v Drought	Aug ’11 v Aug ‘12	C:N	B>A	.0637	Do not reject
Normal v Drought	Aug ’13 v Aug ‘12	C:N	B>A	.0127	Reject

Table 6: Wilcoxon Rank Sum test results for the bottom PM and POC concentrations and C:N based on bottle sample measurements. “Reject” indicates that the null hypothesis is to be rejected and the alternative hypothesis is confirmed. For these tests, POC concentrations for June and August of 2011 and June of 2014 will not be considered, as well as C:N ratios from June 2014 due to differing processing of POC concentrations.

A vs B	Location	Variable	Alternate Hyp	P-Value	Decision
June v August - 2011	Top	PM	A>B	.7972	Do not reject
June v August - 2012	Top	PM	A>B	.8930	Do not reject
June v August - 2013	Top	PM	A>B	.0159	Reject
June v August - 2012	Top	POC	A>B	.0179	Reject
June v August - 2013	Top	POC	A>B	.0001	Reject
June v August - 2011	Top	C:N	B>A	.0006	Reject
June v August - 2012	Top	C:N	B>A	.4646	Do not reject
June v August - 2013	Top	C:N	B>A	.0018	Reject

Table 7: Wilcoxon Rank Sum test results for the surface PM and POC concentrations and C:N for the months of June and August based on bottle sample measurements. "Reject" indicates that the null hypothesis is to be rejected and the alternative hypothesis is confirmed. For these tests, POC concentrations for June and August of 2011 will not be considered due to differing processing of POC concentrations.

A vs B	Location	Variable	Alternate Hyp	P-Value	Decision
June v August - 2011	Bottom	PM	A>B	.3171	Do not reject
June v August - 2012	Bottom	PM	A>B	.9787	Do not reject
June v August - 2013	Bottom	PM	A>B	.0028	Reject
June v August - 2012	Bottom	POC	A>B	.1233	Do not reject
June v August - 2013	Bottom	POC	A>B	.2613	Do not reject
June v August - 2011	Bottom	C:N	B>A	.0003	Reject
June v August - 2012	Bottom	C:N	B>A	.1074	Do not reject
June v August - 2013	Bottom	C:N	B>A	.0867	Reject

Table 8: Wilcoxon Rank Sum test results for the bottom PM and POC concentrations and C:N for the months of June and August based on bottle sample measurements. "Reject" indicates that the null hypothesis is to be rejected and the alternative hypothesis is confirmed. For these tests, POC concentrations for June and August of 2011 will not be considered due to differing processing of POC concentrations.