

**Spatiotemporal Analysis of Ecosystem Degradation
in a Gulf of Mexico Estuary System**

by

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Abstract

Coastal estuaries are a vital resource that provide many environmental and socioeconomic benefits. Despite their value, increased anthropogenic influence has resulted in ecosystem degradation due to eutrophication in coastal estuaries. This study utilizes paleolimnological techniques and spatial analysis to determine the history and extent of anthropogenic impact in a Gulf of Mexico estuary system. The results indicate a significant increase in nutrient, element, and photopigment deposition with increasing anthropogenic influence. Eutrophication was driven by a multiplicity of drivers, but nutrient loading and hydrologic alteration have had the greatest effect on primary producer ecology. Spatial analysis suggests sediment nutrient concentrations are heavily influenced by nearby land-use and point source pollution although variables tied to freshwater inflow such as flow rate, dissolved organic carbon, and salinity appear to have a greater impact on the spatial distribution of phytoplankton communities and abundance.

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List of Abbreviations

Allo	Alloxanthin
B-Car	Beta-carotene
C:N	Carbon-Nitrogen Ratio
Canth	Canthaxanthin
Chl-a	Chlorophyll-a
Chl-x	Unidentified Chlorophyll
Diato	Diatoxanthin
Fuco	Fucoxanthin
GWR	Geographically Weighted Regression
LOI	Loss-On-Ignition
mSQGQ	mean Sediment Quality Guideline Quotient
N	Nitrogen
OC	Organic Carbon
P	Phosphorus
PB12	Perdido Bay Sediment Core
SQG	Sediment Quality Guideline
Total	Total Chlorophylls
WB1	Wolf Bay Sediment Core
Zea+Lut	Zeaxanthin + Lutein

Chapter 1: Background and Purpose

1. Estuaries and Ecosystem Services

Estuaries are one of the world's most productive ecosystems and provide a variety of important ecosystem services. Coastal and estuarine ecosystems, for instance, provide shoreline stabilization and storm protection by attenuating waves and buffering winds which can protect humans from property damage, injury, and death in extreme instances (Barbier 2015). These ecosystems also sequester carbon and improve water quality due to biogeochemical processes that occur between the water column, sediments, and primary producers in the coastal environment (Barbier et al. 2011). Biologically, seagrass beds, salt marshes, oyster reefs, and mangrove forests often located within or bordering estuaries provide vital habitat and food sources for fish populations and other fauna of ecological and economic importance. (Whitfield 2017). However, due to human and climate influence, estuaries are degrading at alarming rates (Doney 2010).

The coastal area lining the Gulf of Mexico contains one of the most extensive estuary systems in the world. This system stretches from the west coast of Florida to the Yucatan Peninsula of Mexico and consists of 39 major estuaries which contains a variety of ecosystems including open water, seagrass beds, salt marshes, oyster reefs, and mangrove forests (Bianchi et al. 1999). These diverse ecosystems provide a plethora of important services, and their benefits have only recently been documented through

research since the turn of the century (Liquete et al. 2013). However, many of these estuaries are changing dramatically due to intense human impacts.

Seagrass meadows in particular are highly valued because of their role as nursery habitat for inshore and offshore juvenile fish species which are of importance to higher trophic levels and humans (Beck et al. 2001). Seagrasses have also been shown to significantly reduce bacterial pathogens in the water column (Lamb et al. 2017). The roots of seagrasses and marsh grasses are known to anchor sediments and slow water velocity which in turn slow erosional processes and stabilize shorelines (de Boer 2007). Oyster reefs contribute to shoreline stabilization, but provide other services including water and sediment filtration (Coen et al. 2007). Additionally, oyster reefs are an important fishery for many coastal areas, particularly in the Gulf of Mexico as production in other areas has declined due to ecological stressors and poor harvest management (Kirby 2004). Grabowski et al. (2012) estimated the value of oyster reefs, excluding harvesting, at between \$5,500 and \$99,000 per hectare per year, a similar valuation to seagrass beds, salt marshes, and mangroves. Despite the value of numerous ecosystem services that coastal estuaries and their surrounding habitat provide, humans are rapidly transforming coastal estuaries as human population and economies in the coastal zone continue to grow (Cloern et al. 2016).

2. Anthropogenic Alteration

Before the turn of the century, Vitousek et al. (1997) claimed human alteration of the environment had been so substantial that we now live on a human-dominated planet. The coastal zone is no exception, and human migration to coastal environments is a

growing trend projected to continue and further alter these ecosystems (Hugo 2011). Humans influence the coastal environment in a variety of ways which could have widespread ramifications including ecosystem shifts, loss of livelihoods, and loss of life and damages from natural hazards and disasters. Mitchell et al. (2015) divide these human impacts on coastal environments into three major classes: stressors that relate to climate change, stressors related to anthropogenic pollution, and stressors related to physical alterations of hydrology.

2.1 Climate Change Stressors

Anthropogenic climate change has lasting, often detrimental, effects on physical and biological systems throughout the biosphere (Rosenzweig et al. 2008). In coastal ecosystems, climate change results in a variety of alterations to natural dynamics including sea level rise, acidification, increased storm frequency and intensity, and changes in precipitation patterns (McGranahan et al. 2007). Mean sea level has risen considerably over the last century and rates are expected to accelerate throughout the 21st century, placing increased stress on coastal environments (Nicholls and Cazenave 2010). Coastal wetlands in particular are highly threatened because increasing water levels and human development along the shoreline prevent inland migration (Runting et al. 2017). Acidity levels are highly variable in coastal environments, but acidification due to increased influence of carbon dioxide can have damaging effects on flora and fauna, especially species that require carbonates such as bivalves (Waldbusser and Salisbury 2014). Increased storm frequency and magnitude in coastal regions negatively impact ecology and can result in loss of vital habitat and the numerous goods and services they

provide (Costanza and Farley 2007). Additionally, the resultant changes in precipitation often result in extreme salinity shifts throughout the water column which can negatively impact biodiversity and biological community structure of coastal ecosystems (Zedler 2010).

2.2 Stressors from Pollution and Eutrophication

Nitrogen and phosphorus loading are typically the biggest pollutants of concern in coastal ecosystems because these elements can cause eutrophication (Anderson et al. 2002). Eutrophication is the intense growth of phytoplankton and cyanobacteria and is predominantly driven by alterations in nutrient inputs, but water depth, salinity, and temperature can also effect eutrophication rates (Hans W. Paerl 2006). Nitrogen and phosphorus can enter a watershed as non-point pollution via runoff from agricultural fields and pastures, but also from urbanized areas as stormwater runoff (Logan et al. 2011). Nitrogen can also enter the water column via atmospheric deposition from the burning of fossil fuels (Hans W. Paerl 1997). Wastewater treatment plants, septic tanks, and straight pipe sewage lines are often additional sources of nutrient loading. Eutrophication causes a variety of effects on coastal estuaries, and the habitats found within, including decreased water quality, hypoxia, and toxin production among others (R. Howarth et al. 2011).

Coastal wetlands are particularly susceptible to the threats of eutrophication. Connell et al. (2017) showed seagrass species were found to react positively to low levels of nutrient enrichment, but when nutrient enrichment crosses a threshold, or “tipping point”, seagrass biomass begins to decline. In addition to seagrasses, salt marshes are also

sensitive to eutrophication. Deegan et al. (2012) found that increased nutrients in the water column cause marsh grasses to concentrate more biomass production in shoot tissue rather than root tissue. This creates vulnerability in marsh grass populations, and a large storm or other stochastic event can significantly reduce marsh grass habitat. Salt marshes, like seagrass meadows, are known nutrient sinks and their decline due to eutrophication creates a positive feedback loop where further decline leads to less nutrient storage and greater eutrophication. Likewise, oyster reefs are at risk of decline due to eutrophication and increased sedimentation rates. Because oysters filter water and consume algal populations therefore acting as a buffer to eutrophication, their decline creates another feedback loop reinforcing a degraded ecosystem state (Nyström et al. 2012).

One aspect of eutrophication of particular concern for coastal environments are the episodic events called harmful algal blooms (HABs) and the subsequent hypoxia that can develop from these events. Harmful algal blooms (HABs) can occur naturally, but prevalence of these events has increased due to anthropogenic alteration of watersheds (Sellner et al. 2003). It is not completely understood how harmful algal species react to variation in nutrient enrichment, but it is known that reactions are species specific (Anderson et al. 2002). HABs can create a variety of problems in a coastal ecosystem including releasing toxic compounds and decreasing benthic oxygen levels in coastal waters (Hans W. Paerl 1997). Hypoxia is the condition caused when water oxygen levels dramatically decrease from organic carbon being aerobically decomposed faster than it can be replaced (Rabalais et al. 2010). Historically, hypoxia does occur naturally, but anthropogenic processes have made the phenomenon more common, especially in coastal

ecosystems (Diaz 2001). Hypoxia can significantly alter an ecosystem because it results in reduced growth rates and mortality among biota thus changing carbon pathways within food webs (Breitburg 2002). In extreme cases, extended severe hypoxia creates dead zones, areas where benthic fauna face fatal conditions and die or are forced into deeper waters (Diaz and Rosenberg 2008). In the Gulf of Mexico, dead zones are attributed to nutrient loading with nitrogen being the biggest concern (Rabalais et al. 2007).

In addition to nutrient enrichment, heavy metals are a pollutant of concern in coastal environments. Heavy metals enter the water column via industrial effluent, sewage, and atmospheric deposition, are toxic to living organisms, and can make commercial fisheries unsuitable for consumption (Bryan and Cole 1971). Contamination requires extended exposure to a heavy metal, but food-chain bioaccumulation can greatly increase the concentration in the tissues of bivalves and predatory species (de Mora et al. 2004). In humans, heavy metal contamination can result in cancer, neurological disorders, and even be fatal (Järup 2003), so heavy metal contamination of fishery populations must be carefully monitored in high-risk areas.

2.3 Stressors due to Physical Alterations

Freshwater inflow is a vital factor of coastal estuary dynamics as it heavily influences the biology and biogeochemical processes within the environment (Sklar and Browder 1998). Despite this importance, humans significantly alter coastal hydrology by dredging passes, building reservoirs, and depleting groundwater storage (Gibson et al. 2003). While these activities are often necessary for human wellbeing and economic productivity, alteration of freshwater flows modifies the flushing rate of estuaries and

results in changes in salinity, nutrient flux, and primary productivity dynamics. Kimmerer et al. (2002) argue that the abundance and survival of estuarine-dependent species increases with increased flow as it dilutes and mobilizes contaminants and increases stratification by decreasing the residence time of water in an estuary. Understandably, these effects can highly influence commercial and recreational fishery populations and their habitat (Gillson 2011).

In addition to affecting water dynamics, sediment transport delivery can be altered by the construction of dams in rivers feeding coastal ecosystems. In fact, Syvitski et al. (2005) state that global sediment transport by rivers is increasing but sediment flux reaching the ocean is decreasing due to the construction of reservoirs. In addition, reservoir construction can severely limit nutrient delivery to coastal ecosystems (Mayer et al. 1998). Sediment and nutrient delivery is vital in coastal ecosystems because it is a source of accretion for wetlands in the fight against sea level rise (Weston 2014). In addition to dam construction, dredging can have a direct impact on environmental quality by reintroducing trapped nutrients, increasing turbidity, and killing benthic biota which can be vital to ecosystem stability (Erftemeijer and Robin Lewis 2006).

3. Purpose of Thesis

The goal of this research project is to determine the extent of anthropogenic impacts (i.e. stressors) on a Gulf of Mexico estuary system. The study area includes coastal two bays, Perdido Bay and Wolf Bay, located along the border of Alabama and Florida, USA (Fig. 1.1). The bays of study have experienced environmental degradation including eutrophication and loss of seagrass habitat, though the causes of decline are

currently debated (R.J. Livingston 2014). The study site will be examined temporally by applying paleolimnological techniques to sediment cores (Fig. 1.2) to recreate historical pollutant (nutrients and heavy metals) inputs and biological responses (phytoplankton abundance and community structure over the past ~200 years. In addition, alterations of organic carbon storage rates before and throughout the period of anthropogenic influence will be investigated. Spatial trends of pollutants and phytoplankton dynamics within the estuary will also be examined using surface sediment samples (Fig 1.2) in an attempt to determine the origins of pollutants, relations to watershed land use, and responses in phytoplankton abundance and community structure using multiple paleolimnological tools and sediment measurements.

3.1 Objectives

The primary research objectives of this study are threefold. (1) Compare conditions of pollutants and phytoplankton communities before and during modern anthropogenic impacts. (2) Discover the time of transition and drivers of degradation, if applicable. (3) Analyze spatial variation in sediments, pollutant hot spots, and links between pollutants and phytoplankton communities. Sediment cores were collected and paleolimnological tools were applied to reconstruct environmental change through time (Obj. 1 and 2, Chapter 2), and similar analyses were applied to an extensive surface sediment survey to determine the modern delivery and distribution of nutrients, metals, and primary producer community structure (Obj. 3, Chapter 3).

3.2 Sediment Science Applications

The primary impetus driving the work conducted for this thesis falls within the sediment sciences. Here, the sustainability and restoration of complex, human-dominated estuaries requires understanding of biogeochemical dynamics and long term monitoring data that is not available for most systems (Baird 2005). However, sediment analysis and paleoecological tools can provide historic data to successfully bridge the knowledge gap in coastal environments. Saunders and Taffs (2009) state that paleoecological sediment techniques can determine pre-impact conditions, the direction and rate of change, drivers of change, and a range of natural variability for the ecosystem in question. Successful paleoecological studies in coastal estuaries are numerous and have been used to study a variety of different anthropogenic alterations.

Logan et al. (2011) utilized paleolimnological sediment techniques to recreate the history of nutrient loading in an Australian estuary to aid environmental managers in decision making for nutrient control in the watershed of the area of study. Bianchi et al. (2002) used paleo-sediment techniques to reinforce the viability of using photosynthetic pigments to recreate long-term eutrophication history in coastal environments. Combining these parameters can be used to determine how nutrient and hydrology alterations affect phytoplankton functional groups and result in the eutrophication of coastal estuaries (Hans W. Paerl et al. 2003). In addition to utilizing sediment cores to create a historic nutrient loading, these techniques can be applied to recreate the industrial legacy of heavy metal contamination in coastal estuaries which can be vital in determining which areas to avoid disturbing at the risk of remobilizing contaminants

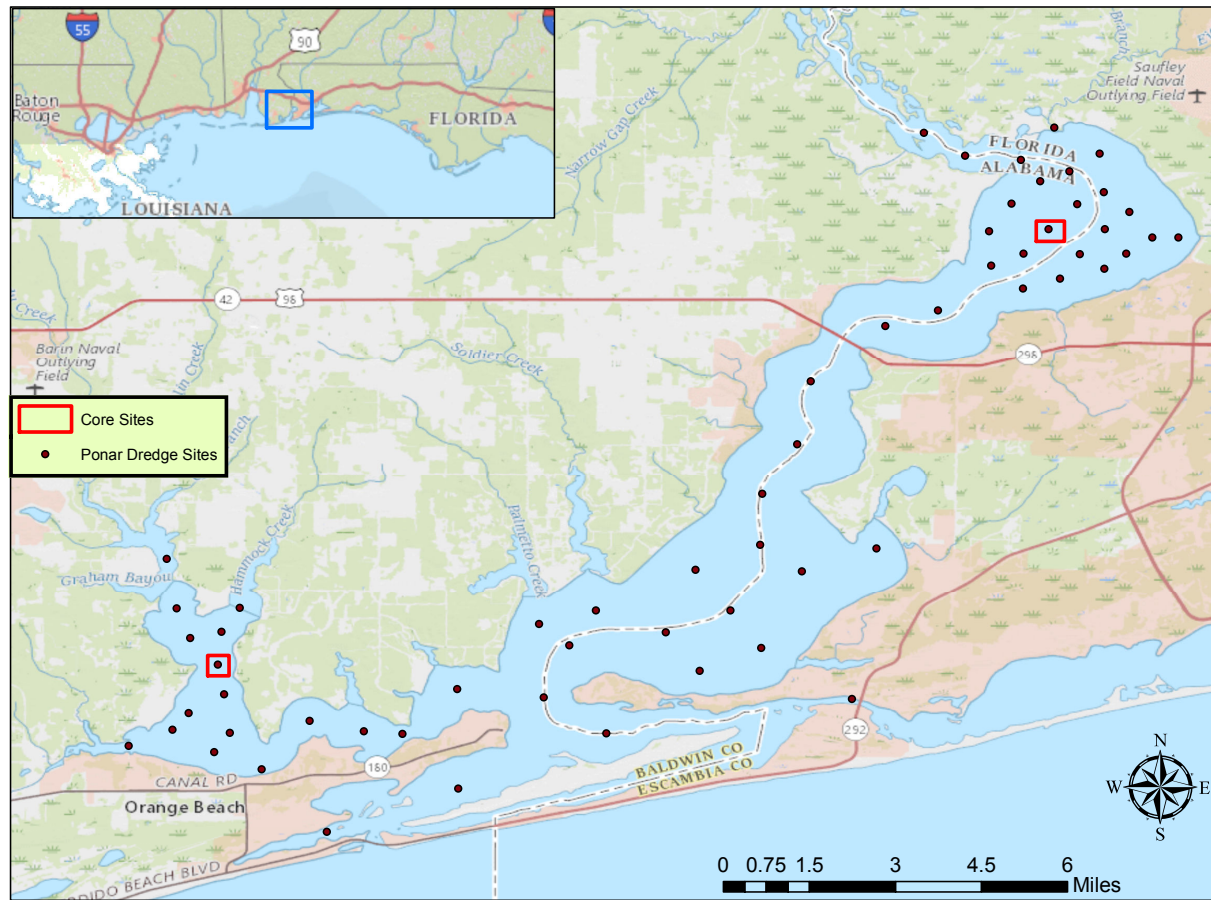
(Reeves et al. 2016). While uncommon, paleolimnological techniques can also be utilized to estimate variation in carbon storage rates across time in open water estuaries, a topic which is not fully understood and requires further research (Jespersen and Osher 2007).

Spatial analysis of pollutant and phytoplankton data in surface sediments and water samples can also result in key findings for management of coastal ecosystems. The anthropogenic impacts to estuary ecosystems are site-specific, vary spatially, and must be understood to understand the dynamics of a particular estuary (Tomasko et al. 2005). Dorado et al. (2015) used water samples to determine that variation of phytoplankton biomass and community structure along the estuary gradient is dependent on freshwater inflows and the variables it influences including total discharge, salinity, and nutrient inputs. Additionally, Sin et al. (1999) found freshwater inflow can alter biogeochemical cycles by demineralizing nitrogen from benthic sediments following spatial patterns.

The influences of land use on nearby coastal waters can also be examined using spatial analyses. Dauer et al. (2000) analyzed the connection between watershed land use and benthic conditions and found correlations to be negative and positive between benthic conditions and urbanization and forestation, respectively. White et al. (2004) also found urban runoff to be detrimental to estuarine health by analyzing spatial trends of nutrient concentration and primary producer abundance. While many of these studies used water samples for data collection, a similar study has validated correlations between nutrient and phytoplankton concentrations in the water column and sediments across space and time (Boyle et al. 2004). In addition to these analyses, it is also possible to measure sediment-bound heavy metal concentrations to determine the extent of anthropogenic influence and biological risks (Birch and Olmos 2008).

This study will combine aspects of the above described paleoenvironmental and spatial analysis studies to determine the spatiotemporal drivers of ecosystem quality across time and space throughout the Perdido Bay estuary system.

Figures



Service Layer Credits: USGS The National Map: National Boundaries Dataset, National Elevation Dataset, Geographic Names Information System, National Hydrography Dataset, National Land Cover Database, National Structures Dataset, and National Transportation Dataset; U.S. Census Bureau - TIGER/Line; HERE Road Data. Data Refreshed July, 2017.

Figure 1.1 Map of the Perdido Bay estuary system and sampling locations. Dots represent sediment surface sample locations and boxes indicate core sites.



Figure 1.2 Pictures of sediment samples. Sediment cores (left) and surface samples (right) were utilized in this study.

Chapter 2: Reconstructing Ecosystem Degradation in a Gulf of Mexico Estuary System Utilizing Paleolimnological Techniques

Abstract: Coastal estuaries provide a variety of ecosystem services important to both the environment and economy of surrounding areas. However, coastal estuaries are highly impacted by anthropogenic alterations and pollution of the water bodies and their watersheds. This study examined ^{210}Pb -dated sediment cores collected from Perdido Bay and Wolf Bay, Alabama, USA to determine the drivers of environmental degradation and the impacts of anthropogenic influence on each bay. Nutrient and photosynthetic pigment (chlorophyll and carotenoid) concentrations were measured to reconstruct a history of nutrient loading and responses in phytoplankton abundance and community structure. The results indicate increasing nutrient pollution beginning in the 1800s and continuing throughout the last century caused increased primary producer abundance throughout the same period. Though anthropogenic inputs appear to have degraded each ecosystem significantly, storage rates of organic carbon have increased ~300% denoting the increased value that estuaries may provide as carbon sinks in eutrophied conditions. The findings of this study showcase the value of paleoecological studies to provide background conditions and drivers of change to better understand the shifting dynamics of coastal estuaries that could assist with ecosystem management and valuation.

Keywords: Estuaries, eutrophication, non-point source inputs, blue carbon

Introduction

Estuaries provide an array of ecosystem services such as water filtration, species habitat, and nutrient storage that result in numerous social and economic benefits (Barbier et al. 2011). However, human stressors in coastal areas are increasing and can negatively impact coastal environments through material inputs, hydrological modifications, industrial pollutants, and eutrophication (McGranahan et al. 2007; Hugo 2011). Eutrophication is the intense growth of phytoplankton and cyanobacteria and is generally associated with changes in nutrient inputs, water depth, salinity, and temperature (Hans W. Paerl 2006). Increased nutrient loading of N and P associated with land use change is typically identified as the primary driver of eutrophication (Anderson et al. 2002). Nitrogen and phosphorus can enter a watershed as non-point pollution from agricultural practices in the form of excess fertilizer, livestock manure, and soil erosion but also from urbanized areas as stormwater runoff or via atmospheric deposition. Point source pollution such as inputs from septic tanks, wastewater treatment plants, and straight pipe sewage lines can be additional sources of nutrient loading. Anthropogenic eutrophication of estuaries has resulted in depletion of species, destruction of habitat, degradation of water quality, and accelerated species invasions (Lotze 2006). Estuarine wetlands in particular are highly vulnerable to eutrophication and are declining despite their immense socioeconomic value (Beck et al. 2001; Deegan et al. 2012; Nyström et al. 2012). Anthropogenic influences can also increase harmful algal blooms (HABs) which can decimate local biology by causing hypoxia or, among certain species, due to their toxicity (Sellner et al. 2003).

Coastal estuaries are dynamic ecosystems integrating inputs from the marine, riverine, and terrestrial environments. River flows and tidal forcing often coexist and create a highly variable ecosystem daily, seasonally, and spatially. The combination of these factors can make it difficult to determine the origin of the drivers of degradation in an ecosystem, and studies have found the source of degradation to differ at site-specific locations. For example, a study by Bianchi et al. (1993) found sediments in the Hudson River estuary to be driven by organic matter inputs from vascular plant detritus upstream while another study by Surratt et al. (2008) used isotopic analysis to determine marine influences were a driving factor in ecosystem change in Apalachicola Bay, Florida, USA. Conversely, Birch and Olmos (2008) observed the effects of local shoreline land use and other anthropogenic inputs on coastal estuaries and found those factors played a significant role in impairing the ecosystems of study. The results of these studies imply that estuaries should be evaluated on a case-by-case basis to determine what pollutants and processes are driving ecosystem degradation and the origins of the pollutants of concern.

Once estuary systems have degraded, a return to the original state requires a decrease of ecological stressors to much lower levels than those of the state change, demonstrating hysteresis in the system (Beisner et al. 2003). This suggests that nutrient concentrations matching those found before the period of degradation are necessary for restoring these habitats to their natural state or preventing further ecological decline. With most estuarine systems experiencing increased impacts through time, decreasing stressors and identifying target levels of historic and natural ecological conditions can be difficult. For most systems historical monitoring data fails to predate disturbance to the

estuary or its watershed. One way to provide data prior to human disturbance and throughout the period of ecological change is to utilize the sediment record and paleolimnological tools (Saunders and Taffs 2009).

Despite estuaries being dynamic environments, paleolimnological techniques in coastal estuaries have been used to provide historic data for multiple systems. Historical sediment deposits have been used to assess changes in nutrient concentrations over time (Weckström et al. 2004; Logan et al. 2011). Bianchi et al. (2002) verified the use of sediments to reflect trends of water column phytoplankton using photosynthetic pigments. The study found pigments a reliable indicator for general increases in phytoplankton biomass and community shifts among plankton. Determining shifts among the functional groups of plankton (chlorophytes, cryptophytes, cyanobacteria, diatoms, and dinoflagellates) has been further understood to reflect water quality and ecosystem structure and function (Hans W. Paerl et al. 2003). Other sediment studies have analyzed inputs of industry (Reeves et al. 2016), nutrients (Surratt et al. 2008), and trace metals (Bojórquez-Sánchez et al. 2017) in coastal estuaries.

Reconstruction of historic environmental data requires a suite of paleolimnological techniques, analyses, and proxies. Loss-on-ignition (LOI) is used as a general indicator of organic matter within a sediment sample (Ball 1964). Carbon to nitrogen molar ratios (C:N) are used to determine the origin of organic material that has been deposited (Meyers and Teranes 2002) with high values (>15) indicating terrestrial inputs, low values (<10) signifying algal inputs, and values in-between denoting a mixture of inputs or macrophyte inputs. Carbon isotopes are also measured to “fingerprint” sediment and determine the source of organic matter (Brenner et al. 1999).

Phytoplankton-derived sediments have lower isotopic values and terrestrial plants have higher values since these primary producers fractionate carbon differently when undergoing different photosynthetic pathways (C3, C4, CAM) (Gearing et al. 1984). Excess-²¹⁰Pb can be used to date sediments and calculate sedimentation rates within the modern era (~150 years) based on a ~22 year half-life and the Constant Rate of Supply model (Appleby and Oldfield 1983). Various photosynthetic pigments (chlorophylls and carotenoids) represent total abundance of algae and cyanobacteria as well as individual primary producer groups (Table 1). In addition to specific pigments being measured, chlorophyll a, pheophytin a, beta-carotene, and total chlorophylls (Total) can serve as indicators of net primary producer abundance. In combination, these tools can provide a significant record of environmental data that cannot be otherwise procured.

In this study, paleolimnological techniques were applied to sediment cores collected from Wolf Bay and Perdido Bay, Alabama, USA to investigate the history of ecosystem degradation which has been recorded since the early 1900s. Due to lack of data, citizens and researchers dispute the cause of water quality decline in the bay system (Livingston 2014). Our study links material inputs (measured as organic matter, nutrients, heavy metals, stable isotopes) with ecosystem responses (photosynthetic pigments) as a cause-effect mechanism of ecosystem condition to further examine the historical environmental conditions of the study area as well as causes of environmental degradation over time. The primary objectives were to (1) create a long-term record of material inputs for each bay and identify the origin of the materials (marine, shoreline, riverine), (2) determine variations in nutrient and heavy metal storage rates between modern and pre-modern sediments, and (3) establish the primary drivers of ecosystem

degradation within the study areas. Moreover, this study provides a novel paleoecological investigation of the eutrophication of a Gulf of Mexico estuary, an under-researched topic of growing importance due to increasing anthropogenic stressors in the region.

Methods

Study Site:

Perdido and Wolf Bays are coastal estuaries located on the border of Florida and Alabama that borders the Gulf of Mexico. Perdido Bay has an area of ~130 km² and a watershed around 3,238 km² (Fig. 2.1) (Altsman and DeMay 2007). The Perdido River is the primary input for Perdido Bay and contributes a majority of the freshwater input into the system. Wolf Bay is a main tributary of Perdido Bay located between Perdido Bay and Mobile Bay. Wolf Bay is a significantly smaller bay with an area of 17 km² and a watershed area of 126 km². The primary inflows for Wolf Bay are the Gulf Intracoastal Waterway from Mobile Bay, two low-order streams to the north, and water from Perdido Bay. Saline water from the Gulf of Mexico enters both waterways from Perdido Pass and from Mobile Bay via the Gulf Intracoastal Waterway.

Land use in the watershed for both bays has historically been dominated by agriculture and silviculture, and septic tanks are very common in the predominantly rural area along in-flow rivers (Schropp 1991). The two counties bordering Perdido Bay (Baldwin, AL and Escambia, FL) have experienced exponential population growth rates from 1800 to the present (Fig. 2.2) as is common in coastal cities throughout the Gulf of Mexico. The city of Pensacola, FL borders Perdido Bay, and a pulp mill located nearby

has been releasing effluent into the bay since the 1940s (Perdido Ecosystem Restoration Group 1998). The city of Foley, AL has recently experienced rapid urbanization in the watershed of Wolf Bay and the cities of Gulf Shores and Orange Beach, which border the southernmost parts of both bays, have experienced similar increases. Recent eutrophication has been attributed to land use change in the system combined with the dredging of the Intracoastal Waterway and Perdido Pass (R.J. Livingston 2014).

Core collection:

One sediment core was collected from both Wolf Bay and Perdido Bay using a piston corer designed to collect undisturbed mud-water interface cores (Fisher et al. 1992). Coring locations were determined based on the results of a soft sediment survey to avoid locations experiencing sediment focusing or erosion to ensure collection of a representative sediment core. The soft sediment survey was performed by forcing a metal rod through the sediment until hitting underlying sand to determine the depth of soft sediments, and surface sediment samples were also collected to measure organic matter content (Whitmore et al. 1996). Both cores were between 78 and 80 cm in length. After collection, cores were sectioned in 2-cm increments and stored on ice for transit to the Auburn University Paleoenvironmental laboratory. Upon arrival, two aliquots of 4.93 cm³ of wet sediment from each section were removed as an archive and for gravimetric analysis (bulk density and loss-on-ignition). The remaining samples were frozen, lyophilized, ground into a homogenous state using mortar and pestle, and sieved at 1 mm to remove large shell material and ensure consistency in further analyses.

Gravimetric Analyses:

A 4.93 cm³ aliquot of wet sediment for each interval was placed into a small pre-weighed crucible and weighed. Samples were dried for 24 hours in a 60°C drying oven and weighed again. Next, samples were burned in a 550°C muffle furnace for three hours to volatilize organic matter as loss on ignition (Hakanson and Jansson 2011). Wet, dry, and ash weights were calculated for each respective category by subtracting the weight of each crucible from the measured weights of the samples at each stage. Loss-on-ignition (LOI) was then calculated using the following formula:

$$\text{LOI} = ((\text{dry-ash})/\text{dry}) * 100$$

LOI is expressed as a percentage of dry mass and bulk density was calculated by dividing the dry weight of each sample by the volume (4.93 cm³) and expressed as g dry cm⁻³ wet.

Sediment Chronology:

Sediments were dated by measuring excess-²¹⁰Pb using a germanium well detector (Appleby et al. 1986). Excess-²¹⁰Pb was measured on each core interval using dried, ground samples until no excess ²¹⁰Pb was detected for three sequential samples (32 cm for both locations). Prior to measurement, sediments were sealed in plastic tubes using epoxy for at least 20 days to allow for secular equilibrium. The Constant Rate of Supply model was used to calculate dates for each section as well as sedimentation rates (Appleby and Oldfield 1983).

Nutrients and Heavy Metals:

Total carbon and total nitrogen were measured on a Costech combustion elemental analyzer with an attached autosampler. Total organic carbon and stable isotopes ($\delta^{13}\text{C}$) were measured using an isotopic mass spectrometry system coupled to a CN analyzer at the University of Georgia Center for Applied Isotope Studies (<https://cais.uga.edu>). Isotope values were determined by comparing to a reference standard of Pee Dee Belemnite and reported using standard delta notation. Prior to analysis of organic carbon (OC) and $\delta^{13}\text{C}$, samples were acidified in HCl acid vapors for 24 hours to ensure removal of inorganic carbon (Harris et al. 2001). Other elements and heavy metal concentrations (P, K, Mg, Ca, S, Mn, Fe, Cr, Pb, Ni, Al, Na, As, and Hg) were calculated on dry sediment using an ARL 3560AES ICP analyzer following acid digestion in a heated block using EPA method 6010B at Waters Agricultural Laboratories (<https://watersag.com>).

Chlorophylls and Carotenoids:

Photosynthetic pigments (chlorophylls and carotenoids) were measured using High-Performance Liquid Chromatography (HPLC) following the methods of Leavitt and Hodgson (2001) and Waters et al. (2015). Dried sediment samples were weighed and extracted at -20°C for 16-20 hours in a solvent mixture containing acetone, methanol, and water at a ratio of 80:15:5. After extraction, samples were centrifuged and filtered at $0.22\ \mu\text{m}$ through a syringe filter to ensure removal of particulate matter. Samples were then placed in an autosampler where they were mixed with an ion-pairing agent at a 3:1 ratio. A $100\ \mu\text{l}$ of sample was injected into a Shimadzu HPLC system following the mobile

phase and time sequence of Leavitt and Hodgson (2001). Chlorophylls and carotenoids were separated using a Phenomenex Luna C18 column and measured by a fluorescence detector and a photodiode array detector, respectively. Pigments were identified by comparison to known retention times and spectra of standards. Final concentrations were expressed as nmol g^{-1} organic matter.

Statistical Analyses:

K-means cluster analysis was performed using LOI, OC, N, P, S, Diato, Canth, and total chlorophylls (Total) to determine significantly different clusters within each sediment core. These variables were chosen for the cluster analysis because they are indicators (LOI, OC, Total) or drivers (N, P) of eutrophication or salt water intrusion (S) (Howarth 1984) or represent changes in water quality (Diato, Canth) or primary producer abundance (Total). In addition, Ca was used in the Wolf Bay core due to the presence of oyster hash in the bottom of the core but was omitted from the cluster analysis for the Perdido Bay core since oyster shells were not collected in that core. This cluster analysis resulted in the partitioning of the sediment cores into time-specific periods that were representative of the environmental conditions of each period and significantly different than other periods. Additionally, correlation coefficients were calculated between OC, N, P, and Total for each core to determine relationships between nutrient inputs and total primary producer abundance.

Storage rates were calculated by multiplying element concentrations by the CRS-determined sedimentation rates for the datable portions of each core. Storage rates were divided into two time periods (~1900 AD to 1950 AD and 1950 AD to present) to

compare storage changes between dateable clusters. Unpaired two-tailed t-tests were utilized to determine significance of distinction between storage rates of analytes. Principal component analyses (PCA) were performed on normalized data using pigment concentrations as an exploratory measure to investigate the presence of community shifts between clusters. Results were then visualized using a biplot of the two most significant principal components as determined by eigenvalue.

Results

Sediment cores collected at each site were predominantly sandy with increasing organic matter upcore, most notably in the top ten centimeters. WB12 contained visible oyster shells from 78 cm to 54 cm. For both the Wolf Bay and Perdido Bay cores, the excess-²¹⁰Pb record reached background supported levels at 32 cm (Fig. 2.3 & Fig. 2.4). Steadily increasing values of excess-²¹⁰Pb from 32cm to the top of each core suggest minimal mixing over time. The CRS model provided deposition dates and sedimentation rates for each core. The average sedimentation rate for WB1 throughout the dateable section of the core was $1780 \pm 663 \text{ g m}^{-2} \text{ yr}^{-1}$ while the calculated average for PB12 was $1204 \pm 600 \text{ g m}^{-2} \text{ yr}^{-1}$.

Four non-overlapping clusters of sediment core sections were identified in WB1 (Fig. 2.5 and Fig. 2.6) using the k-means cluster analysis. Cluster 1 (n=9) consists of the top 18 cm of the core and is representative of the most modern conditions (1978-2017 AD). This cluster contains the highest concentrations of OC, N, P, diato, and chl-a. Cluster 2 (n=6) consists of 30-18 cm (1927-1977 AD) and appears to signify a transitional state between Clusters 1 and 3, as many measured concentrations fall

between values of those clusters. Cluster 3 (n=14) consists of 58-30 cm and represents the period of time preceding intense human impacts and is inferred as pre-disturbance conditions. Cluster 4 (n=10) consists of 78-58 cm and represents the remains of a historic oyster reef as indicated by direct observation and the high concentration of Ca. Loss on ignition, OC, N, and P follow a similar stratigraphic trend of linear increase throughout the core, and $\delta^{13}\text{C}$ decreases steadily. Pigments are only dominant in Clusters 1 and 2 with the exception of Canth and B-Car, which are present in significant quantities throughout the core. Lut+Zea, Canth, B-Car, and Chl-a see a dramatic shift (2x concentration increase) between Clusters 2 & 3 (30 cm); Allo and Diato also increase considerably but do so later in Cluster 2 (22-26 cm).

Three clusters were identified in PB12 by k-means cluster analysis (Fig. 2.7 & Fig. 2.8): Cluster A (n=12, top 26 cm), Cluster B (n=16, 54-26 cm), and Cluster C (n=13, 80-54 cm). A fourth cluster was not needed due to the lack of an oyster layer in the Perdido Bay core. Clusters A (1939-2017 AD) and B (pre-1864-1938 AD) show a steady increase in pigment concentrations through time while Cluster A shows higher concentrations in nutrient inputs and phytoplankton abundance in the age of modern influence. Cluster C was inferred as a historic non-depositional zone (low LOI, high BD, and near-zero pigment concentrations) so data from this cluster are ignored in further discussion. LOI, OC, N, P, and S follow a steady, increasing trend throughout the core along with all measured pigment concentrations.

Storage rates of measured nutrients and heavy metals all increased by an average of 195% post-1977 in WB1 (Table 1) and an average of 338% post-1938 in PB12 (Table 2) when compared to respective concentrations in previous dateable clusters. Within the

dateable records, deposition of measured elements was found to be statistically different ($p < .05$) between clusters in each core (Table 1, Table 2, Fig. 2.9, and Fig. 2.10).

Correlation coefficients between OC, P, N, and Total ranged between 0.82 and .98 for WB1 (Fig. 2.11) and .66 and .94 for PB12 (Fig. 2.12). The correlation coefficient between OC, N, and P was greater than 0.9 for each combination in WB1 and PB12 for all clusters. Correlation between P and Total was greater than N and Total in WB1 (.85 > .82) while the converse was true in PB12 (.66 < .73). The relationship between N:P and Total in WB1 appears to follow an asymptotic trend while a pattern between N:P and Total is not as clear for PB12.

Principal component analysis of pigment concentrations provided ordination of core sections by cluster for WB1 with modern samples (Clusters 1 and 2) ordinating together (Fig. 2.13). Principal component 1 explained 80.6 % of variance in the dataset and principle component 2 explained 8.4 %. Diato, Chl-a, Chl-b, and Allo ordinated with Cluster 1, and Cluster 2 aligned more with vectors for Canth, Pyro, and B-Car. PCA was also run for PB12, but no distinct ordination with particular variables was observed between clusters.

Discussion

The sediment cores from Wolf Bay and Perdido Bay recorded the period of human development as well as the period of pre-disturbance conditions based on the excess-²¹⁰Pb dating model and other stratigraphic markers. Both cores indicated evidence of modern eutrophication linked to the period of increased human disturbance and land use change. Increased nutrient inputs (C, N, P) coordinated with the beginning of intense

agricultural development within each watershed (Mitchell 2019). Primary producer responses to increased anthropogenic nutrient loading occurred in both bays, but Wolf Bay showed a delayed response. The current state of the estuaries indicated from sediment data are consistent with modern water quality data (Robert J. Livingston 2007) and the current condition of both bays (Alabama Department of Environmental Management 2014), reaffirming the accuracy of collected sediment data. The importance of watershed land use on coastal bays is reflected in the changes in nutrient, heavy metal, and photopigment deposition throughout the sediment core profiles and provide distinct insight on the history, changing storage dynamics, and eutrophication of the study area.

Nutrient and Elemental Inputs and Deposition

Observed changes in nutrient deposition indicate a considerable transformation in watershed land use throughout the reconstructed history of both sediment cores. C:N values (>20) indicate that terrestrial material is the source of a large portion of sediment delivery in historic sediments of upper Perdido Bay, but modern sediment calculations indicate that aquatic primary producers (phytoplankton) have become an increasingly important input as shown by decreases in C:N values (Fig. 2.8). Wolf Bay C:N measurements (Fig. 2.6) remain relatively unchanged throughout the sediment record (16.04 ± 2.27) indicating riverine inputs from watershed land use are not as dominant a factor historically as they were in Perdido Bay. Unlike Perdido Bay, Wolf Bay lacks a major riverine input, which would lessen the influence from terrestrial and riverine producers. Prior to the excess- ^{210}Pb record in each core, measured nutrient concentrations were significantly lower than samples in the modern era. However,

nutrient concentrations began to increase in the 20 cm prior to the beginning of the excess-²¹⁰Pb record in each core (~1800s), indicating an influx of nutrients before modern large-scale human disturbance. European settlement that included largescale agricultural practices in the area began in the 1700s and early 1800s (Weddle 2014) and aligns with the noted nutrient influx. Increased erosion from the clear cutting of trees and introduction of row crop agriculture synonymous with early European settlement is most likely the cause of the initial increases in nutrient concentrations found in sediment deposited before the excess-²¹⁰Pb records. Cluster 3 in Wolf Bay and Cluster B in Perdido Bay show increases in many measured sediment parameters including nutrients and heavy metals and likely reflect the continued importance of agriculture in the region in the early 1900s and the beginning of industrial influence. The most recent sediments in WB1 and PB12 contain the highest concentrations measured in all parameters throughout the cores and represent the period of 1974-present in Wolf Bay and 1931-present in Perdido Bay. In the twentieth and early twenty-first centuries, the county has experienced urbanization, particularly along the shorelines of the ocean and bays. Observed variations in sediment quality (N, P, heavy metals) can be primarily attributed to the effects of agriculture and industry due to dramatic increase in population and development from 1960 until today (Wilson and Fischetti 2010); both bays reflect the multiplicity of stressors impacting most coastal systems. Throughout each of these time periods and respective clusters, changes in sediment dynamics reflect the eutrophication and overall ecosystem degradation that has been documented in the study areas (Altsman and DeMay 2007; Robert J. Livingston 2007; Wang and Kalin 2018)

Carbon Sequestration

In addition to total sediment deposition, OC storage also showed distinct changes through time for each bay. In this study, unvegetated, open-water estuary sediments were found to average around $81 \pm 23 \text{ g C m}^2 \text{ yr}^{-1}$ in Wolf Bay and 80 ± 37 in Perdido Bay throughout the most modern clusters (WB1 Cluster 1 and PB12 Cluster A). Maximum storage rates up to $150 \text{ g C m}^2 \text{ yr}^{-1}$ were calculated for certain sections within the top cluster of each core. McLeod et al. (2011) calculated similar storage rates in coastal vegetated aquatic habitats; seagrass meadow storage in particular was estimated at $138 \pm 38 \text{ g C m}^2 \text{ yr}^{-1}$. These findings signify similar rates of carbon sequestration are possible in eutrophied non-vegetated ecosystems as vegetated ecosystems. This inference aligns with the findings of other non-vegetated estuarine OC burial research, though few studies exist because estuaries are often ignored as carbon sinks despite being one of the most productive ecosystems on Earth (Jespersen and Osher 2007; Millar et al. 2015).

Previous studies on carbon storage in open-water aquatic systems have largely favored inland waters. In a study by Dean and Gorham (1998) it was estimated that large lakes sequester $5 \text{ g C m}^2 \text{ yr}^{-1}$, small lakes sequester $72 \text{ g C m}^2 \text{ yr}^{-1}$, and that reservoirs sequester $400 \text{ g C m}^2 \text{ yr}^{-1}$. The findings of this study indicate the possibility that coastal estuaries may be storing carbon at significant rates compared to other aquatic ecosystems. Furthermore, Heathcote and Downing (2012) compared carbon storage rates in historic and modern lake sediments and found a 4.5x increase in carbon storage post-eutrophication in a study of midwestern lakes. Our study found 3x increases within historic clusters in each system and indicate that a similar phenomenon could be present in coastal estuary ecosystems. The findings of this study indicate the carbon storage

potential of estuaries should be further studied along with the possible impacts on the global carbon budget.

Eutrophication & Drivers

Following the nutrient increases in deposition, photopigments showed a response in primary producer abundance to the incoming nutrients. N is known to be the most common limiting nutrient for primary productivity in shallow-water coastal estuary environments (R. W. Howarth and Marino 2006), but N & P have been determined to co-limit net primary production in certain lower latitude estuaries (Rudek et al. 1991; Fisher et al. 1999). Data from the Wolf Bay sediment core indicate primary producer abundance is more closely linked to P inputs than N. N:P molar ratios decrease over time due to increased P loading, and total fluorescence values are only high in recent periods with low N:P ratios. The increase in N storage in older sediments for both bays could indicate an historic abundance of N in the system. Denitrification could explain the decrease in N:P ratios, but the high correlation ($R > .9$) of N to P, OC, and total fluorescence (Fig. 2.11) throughout the cores suggests that measured N has entered the system as organic matter and stored at similar rates over time. N:P decreases have also been noted in other sediment core studies where P inputs dramatically increase (Waters et al. 2018) or eutrophication occurs from P inputs (Harmon et al. 2014). Likewise, Yan et al. (2016) noted a trend of N:P decreases in sedimentary environments due to faster accumulation of P than N in human impacted aquatic ecosystems. While P is not the expected limiting nutrient in most coastal ecosystems, the findings of this study indicate it could be an important factor of eutrophication in Wolf Bay, aligning with other Gulf of Mexico

studies that have found estuaries to be P-limited (Bianchi et al. 1999). However, we recognize the dynamic nature of the estuarine environment means a combination of many factors play a role in determining the ecological state of this ecosystem.

This study suggests that eutrophication has been driven by a multiplicity of drivers in both Wolf and Perdido Bays. While nutrient dynamics appear to be the primary driver of ecosystem degradation in this study, other secondary drivers appear to play contributing roles in driving ecological characteristics. Changes in hydrology can alter primary producer dynamics in estuaries. For example, the nearby Apalachicola Bay has experienced environmental decline from upriver dams decreasing freshwater inputs and increasing marine influence on the system (Surratt et al., 2008). The flow of the Perdido River is not significantly impeded by major anthropogenic dams, but continual dredging of Perdido Pass and the Gulf Intracoastal Waterway have played a significant role in altering residence times and tidal forcing dynamics in both study areas (Devkota and Fang, 2015).

Construction of the Gulf Intracoastal Waterway, connecting Mobile Bay and Pensacola Bay through Wolf Bay and Perdido Bay in 1934 (Alperin 1983), also appears to have heavily impacted phytoplankton ecology in Wolf Bay which showed a lag time between nutrient input increase and increasing phytoplankton abundance while Perdido Bay experienced a more immediate response to nutrient inputs. Significant increases in photopigment concentrations in the sediment record between Cluster 2 and Cluster 3 can be recognized in the early 1930s and imply that increased connectivity with Mobile Bay heavily contributed to the eutrophication of Wolf Bay. This phenomenon could be explained by variations in an unmeasured variable such as salinity or a shift in hydrology

and explains the sudden shift in primary producer community and abundance as well as the lag between nutrient inputs and eutrophication. In Perdido Bay, the dominant freshwater influence that the Perdido River exerts on the upper bay also appears to be a driver of ecosystem quality. This upper bay has higher flushing rates and water velocity and is the least saline portion of the entire study area (Xia et al. 2011), and salinity is known to have a major effect on phytoplankton community structure in coastal estuaries (Dorado et al. 2015). The water column of the upper bay also has notably more dissolved organic carbon (DOC) (Macauley et al. 1995) than the rest of the study area indicating light attenuation may be a limiting factor for primary productivity in the upper bay.

The sediment record reconstructed from Wolf Bay indicates cyanobacteria may have been present in the system in a historic, pre-eutrophied state (pre-1906) due to the prevalence of canthaxanthin throughout the sediment record (Fig. 2.6). Canthaxanthin is a diagnostic pigment for cyanobacteria and has been shown to successfully reconstruct historic cyanobacteria communities (Leavitt and Hodgson 2001, Waters et al. 2015). In modern sediments, it appears a second shift in pigments has occurred between the most recent clusters. The biplot of the PCA (Figure 2.13) indicates that the modern sediment has been more influenced by diatoms and cryptophytes than the previous cluster, which appears to have had more impact from cyanobacteria. Green & siliceous algae appear to have been steadfast throughout the eutrophied state of Wolf Bay. In most systems, eutrophication typically results in an increase of cyanobacteria in the water column, so these findings suggest a different biological reaction to changing environmental conditions. In Perdido Bay changes in community structure were less evident as all measured pigments seem to react to material inputs in a similar fashion, which could be

linked to the higher flushing rate and potential light attenuation known in the Perdido Bay system.

Conclusion

Our sediment core data suggest Wolf and Perdido Bays have experienced eutrophication from changes in land use, urbanization, and hydrology in the last century. As a result, the current phytoplankton dominated system is promoting habitat homogeneity (Altsman and DeMay 2007) and alterations to the biological community. These outcomes provide some insight on how multiple factors affect the environmental and ecological status in similar ecosystems. This study also provides estimates of OC burial rates in Gulf of Mexico open-water estuaries. These values are comparable to other high-carbon storage systems such as salt marshes, mangrove swamps, and seagrass meadows (McLeod et al. 2011). Estuary carbon storage rates should be further researched throughout the Gulf of Mexico to improve understanding of the valuation of these ecosystems and their significance in global carbon budget calculations. Furthermore, it is imperative that the effects of eutrophication on past and present carbon storage rates are included in estimations of future storage rates as eutrophication becomes more common in these environments.

Overall, this study confirms the greater usefulness of a paleoecological record in coastal estuaries, an increasingly important, resource-rich ecosystem, as humans continue to move towards the coast and increase environmental stressors in these environments. Studies such as this provide background conditions of the environment that would be otherwise unavailable and offer potential explanations for sudden incidents of otherwise

unexplainable degradation. Equipped with historic environmental data provided by a paleo-study, environmental agencies should be better outfitted with essential information to create a more efficient plan for management and valuation of the coastal zone in the Gulf of Mexico and beyond.

Tables

Table 1. List of abbreviations for photosynthetic pigments and respective phytoplankton class or abundance indicators.

	<i>Pigment</i>	<i>Phytoplankton Indicator</i>
<i>Allo</i>	Alloxanthin	Cryptophytes
<i>Diato</i>	Diatoxanthin	Diatoms
<i>Lut</i>	Lutein	High-order plants
<i>Zea</i>	Zeaxanthin	Cyanobacteria
<i>Canth</i>	Canthaxanthin	Cyanobacteria
<i>B-Car</i>	beta-Carotene	Primary Producer Abundance
<i>Chl-a</i>	Chlorophyll-a	Primary Producer Abundance
<i>Total</i>	Total Chlorophylls	Primary Producer Abundance

Table 2. Elemental deposition rates for WB1 expressed in $\text{g m}^2 \text{yr}^{-1}$. P-value indicates significant difference in rates between clusters. Increase is expressed as average percent increase between clusters.

Element	Dated History 1927-2017	Cluster 2 1927-1977	Cluster 1 1978-2017	p-value	% Increase
C	60.0 ± 32.7	28.2 ± 8.59	81.2 ± 23.6	0.000079	288
N	4.38 ± 2.33	2.15 ± 0.807	5.86 ± 1.70	0.000104	272
P	0.576 ± 0.312	0.271 ± 0.116	0.779 ± 0.212	0.000051	288
K	3.75 ± 1.31	2.52 ± 0.730	4.57 ± 0.868	0.000330	181
Mg	8.32 ± 3.11	5.37 ± 1.60	10.3 ± 2.10	0.000209	192
Ca	4.45 ± 1.94	2.61 ± 1.26	5.68 ± 1.17	0.000704	218
S	27.8 ± 9.50	18.6 ± 5.29	33.9 ± 5.99	0.000241	182
Mn	0.405 ± 0.115	0.311 ± 0.119	0.468 ± 0.0577	0.020992	151
Fe	32.5 ± 10.3	22.4 ± 5.92	39.2 ± 6.06	0.000231	175
Cr	0.0555 ± 0.0145	0.0419 ± 0.0072	0.0646 ± 0.0101	0.000219	154
Pb	0.0427 ± 0.0143	0.0291 ± 0.006	0.0518 ± 0.0103	0.000131	178
Ni	0.0121 ± 0.0038	0.00842 ± 0.0019	0.0145 ± 0.0026	0.000146	172
Al	31.6 ± 10.2	21.6 ± 5.91	38.2 ± 5.98	0.000251	177
Na	29.2 ± 15.5	15.6 ± 5.79	38.3 ± 12.9	0.000603	246
As	0.0316 ± 0.0102	0.0216 ± 0.0059	0.0382 ± 0.006	0.000251	177
Hg	0.0292 ± 0.0155	0.0156 ± 0.0058	0.0383 ± 0.0129	0.000603	246

Table 3. Elemental deposition rates for PB12 expressed in g m² yr⁻¹. P-value indicates significant difference in rates between clusters. Increase is expressed as average percent increase between clusters.

Element	Dated History <i>1864-2017</i>	Cluster B <i>1864-1938</i>	Cluster A <i>1939-2017</i>	p-value	% Increase
C	66.1 ± 39.9	25.7 ± 12.0	79.6 ± 36.6	0.00058	309
N	4.1 ± 3.0	1.1 ± 0.5	5.1 ± 2.8	0.00032	484
P	0.48 ± 0.31	0.15 ± 0.08	0.59 ± 0.27	0.00019	393
K	2.4 ± 1.6	0.9 ± 0.3	2.9 ± 1.5	0.00065	333
Mg	7.5 ± 5.1	2.5 ± 0.9	9.2 ± 4.8	0.00046	373
Ca	3.5 ± 2.5	1.2 ± 0.5	4.3 ± 2.3	0.00081	358
S	24.8 ± 13.5	8.7 ± 3.9	30.1 ± 10.9	0.00005	345
Mn	0.132 ± 0.080	0.033 ± 0.018	0.165 ± 0.062	0.00001	505
Fe	18.9 ± 9.1	9.9 ± 2.8	21.8 ± 8.5	0.00089	219
Cr	0.051 ± 0.028	0.020 ± 0.009	0.062 ± 0.023	0.00012	316
Pb	0.029 ± 0.015	0.012 ± 0.007	0.035 ± 0.013	0.00174	279
Ni	0.008 ± 0.005	0.003 ± 0.001	0.010 ± 0.004	0.00006	395
Al	21.8 ± 12.1	8.0 ± 3.8	26.4 ± 10.2	0.00014	332
Na	15.3 ± 16.2	4.9 ± 2.0	18.8 ± 17.4	0.01934	382
As	0.0218 ± 0.012	0.0080 ± 0.004	0.0264 ± 0.0102	0.00014	332
Hg	0.0153 ± 0.016	0.0049 ± 0.002	0.0188 ± 0.0174	0.01934	382

Figures



Figure 2.1. Map of Study Area and Core Sites. Green squares indicate coring locations. Inset map shows the Gulf of Mexico bordering the coasts of Louisiana, Mississippi, Alabama, and Florida from west to east.

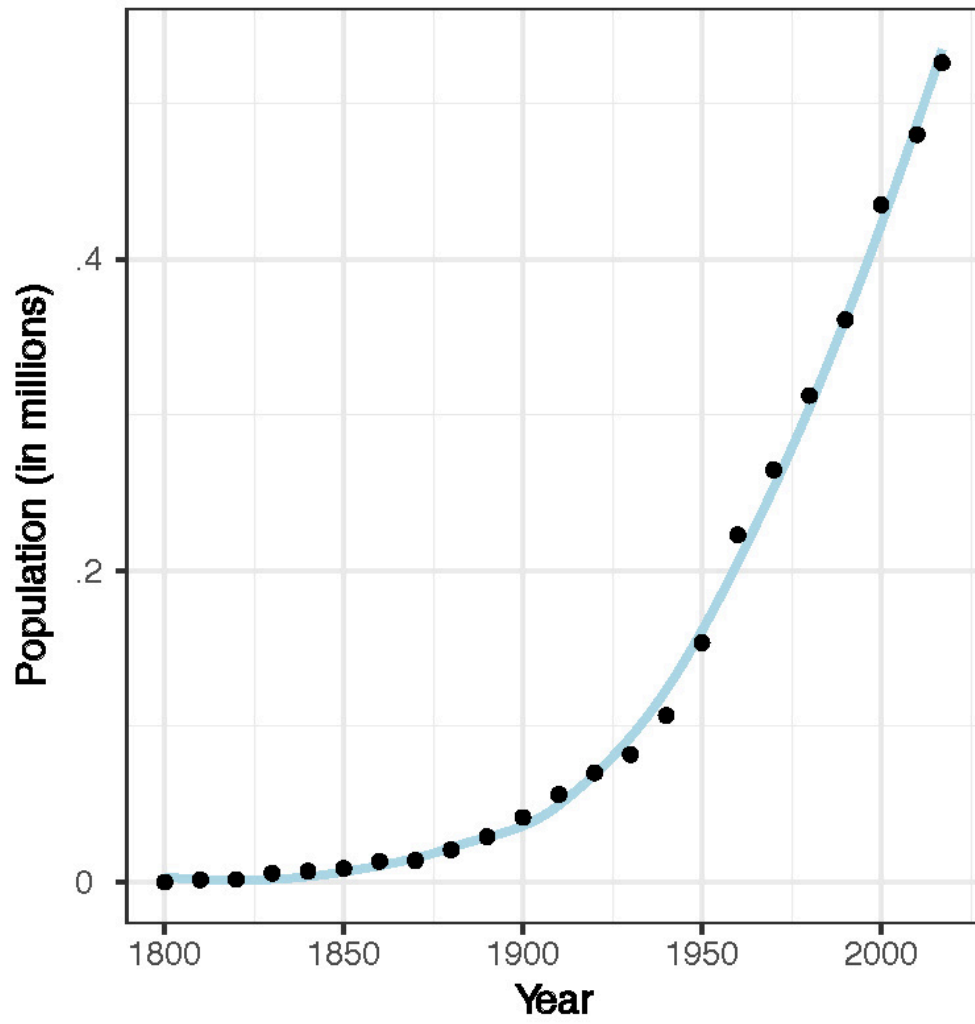


Figure 2.2. Combined populations of Baldwin County, AL and Escambia County, FL from 1800 to 2017, provided by the US Census Bureau. A LOESS curve is applied to provide a smooth trendline.

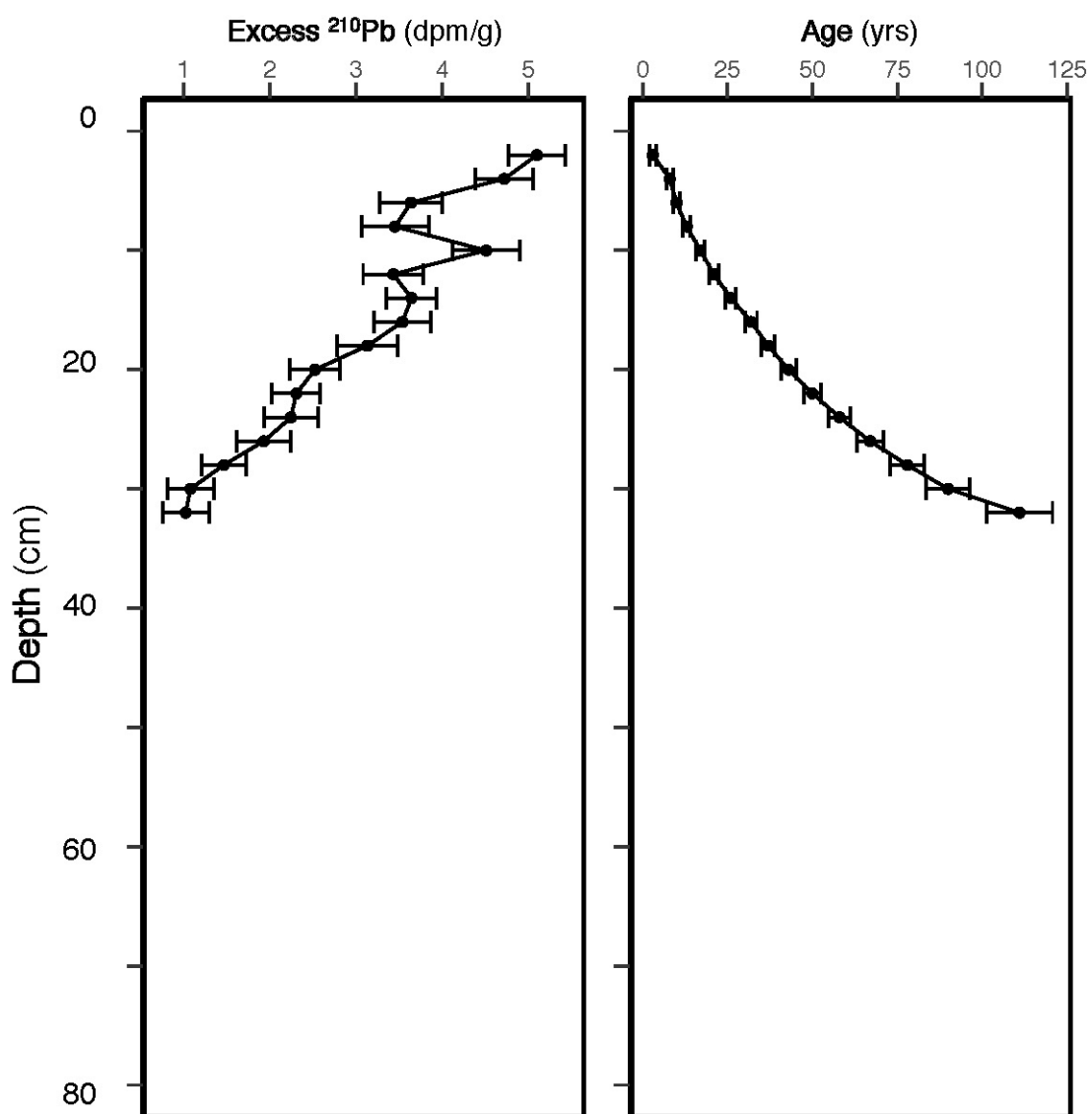


Figure 2.3. Dating model for WB1. Excess ^{210}Pb (left panel) and age (right panel) are plotted versus depth. Error bars indicate one standard deviation of calculated excess ^{210}Pb (left) and age (right) values. Total length of sediment core was 78 cm.

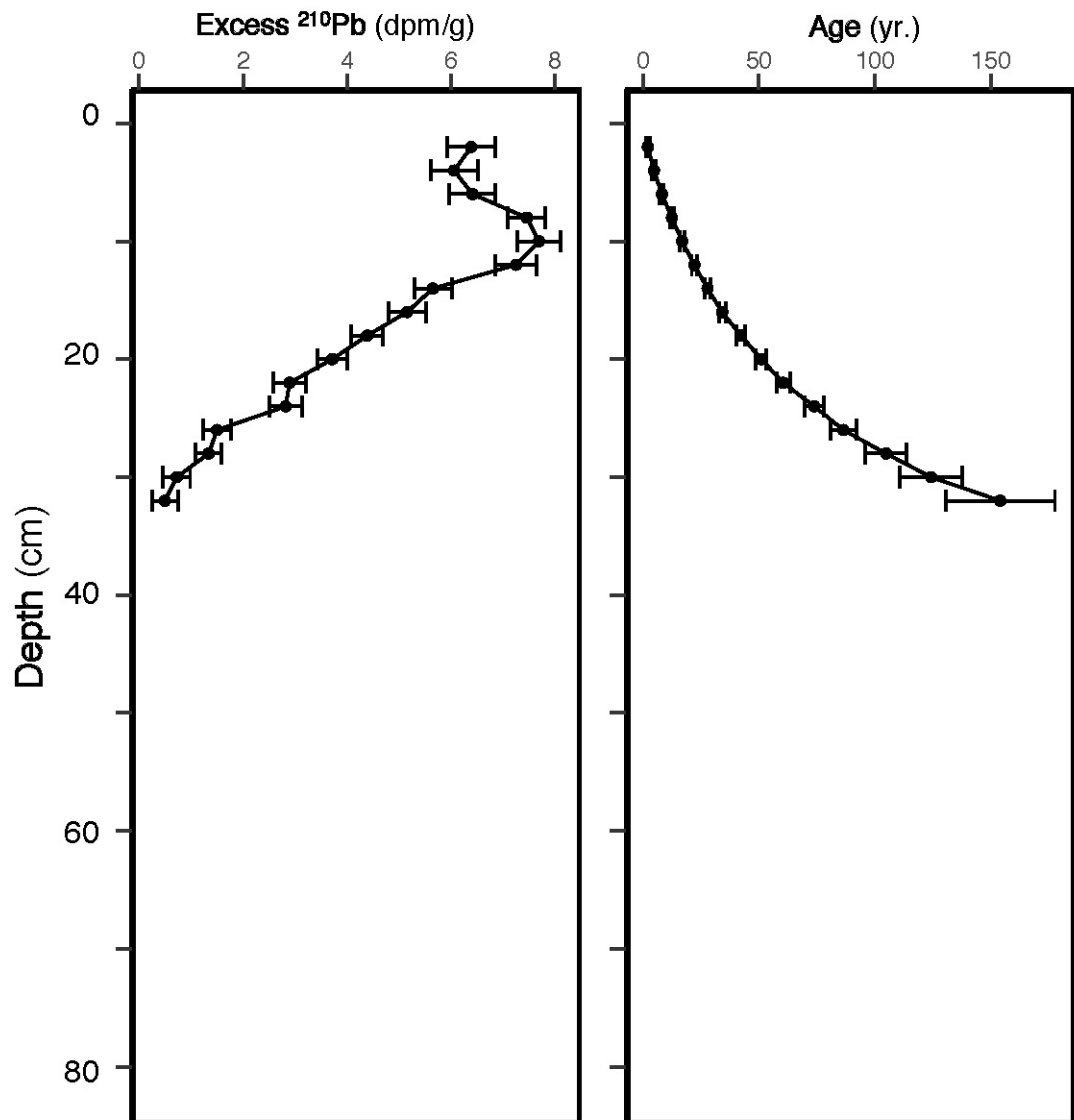


Figure 2.4. Dating model for PB12. Excess ²¹⁰Pb (left panel) and age (right panel) are plotted versus depth. Error bars indicate one standard deviation of calculated excess ²¹⁰Pb (left) and age (right) values. Total length of sediment core was 80 cm.

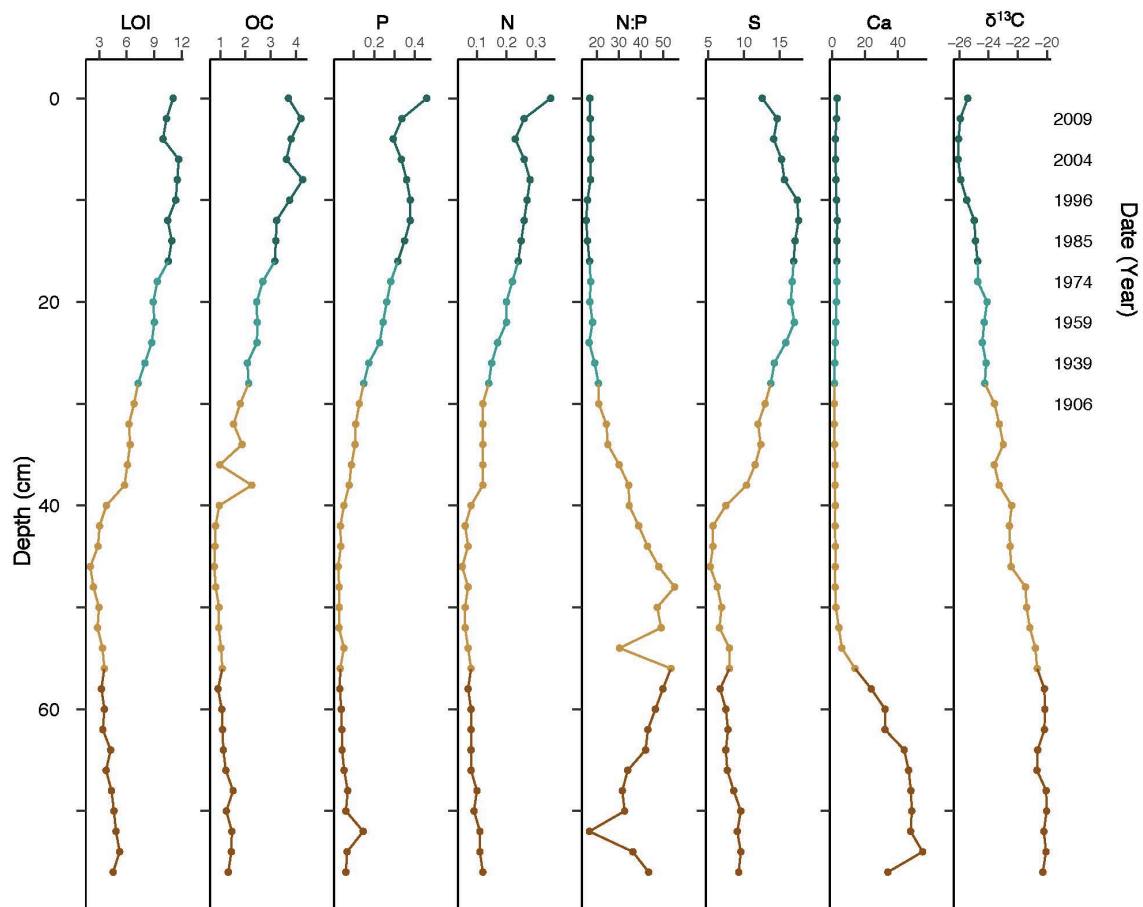


Figure 2.5. Core profiles of inputs for WB1. Loss on ignition (LOI), organic carbon (OC), and nitrogen (N) reported in percent. N:P is expressed as a molar ratio. Phosphorus (P) and sulfur (S) measured in mg g⁻¹. δ¹³C expressed in ‰. Each color signifies a different cluster determined via k-means cluster analysis.

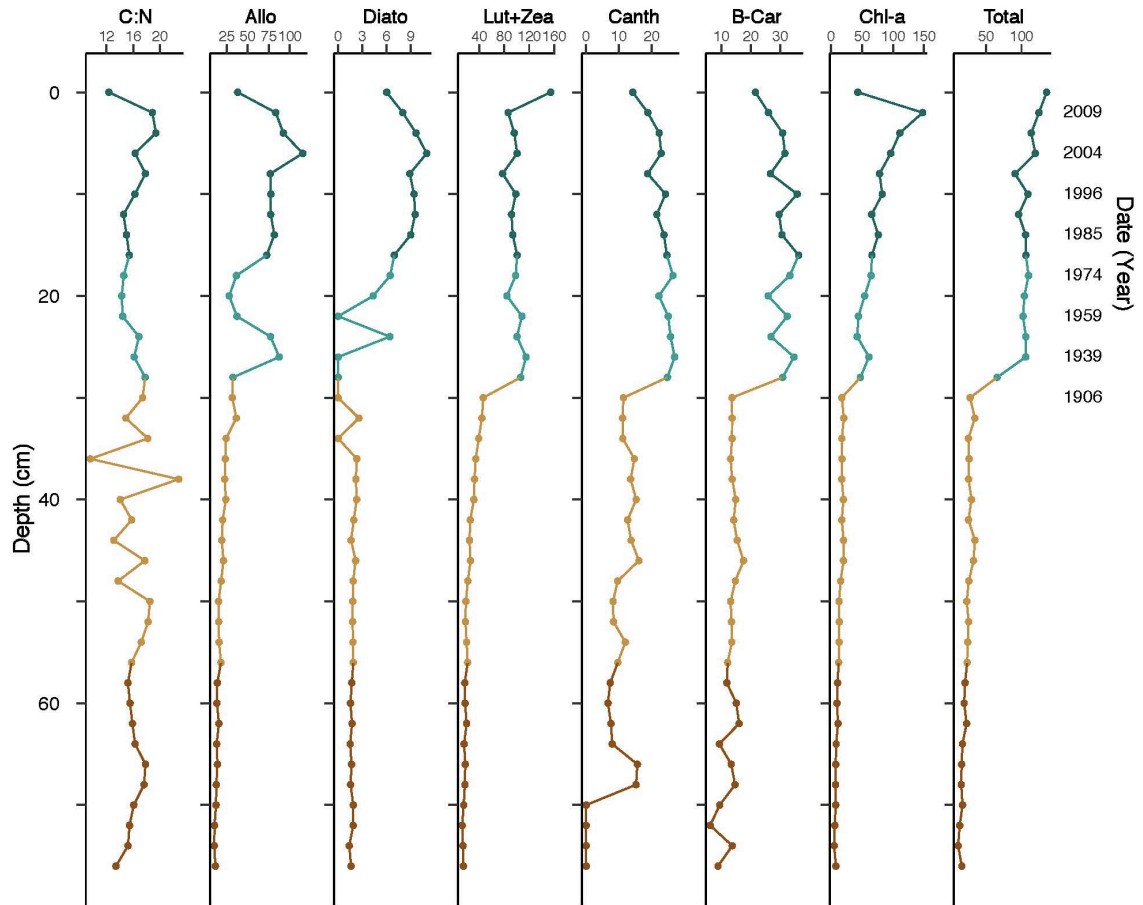


Figure 2.6. Core profiles of biologic variables for WB1; variables represent biological responses to increased nutrient inputs. Carbon-nitrogen (C:N) expressed as a molar ratio. Photosynthetic pigments (Allo, Diato, Lut+Zea, Canth, B-car, Chl-a) are reported as nmol/g organic matter.

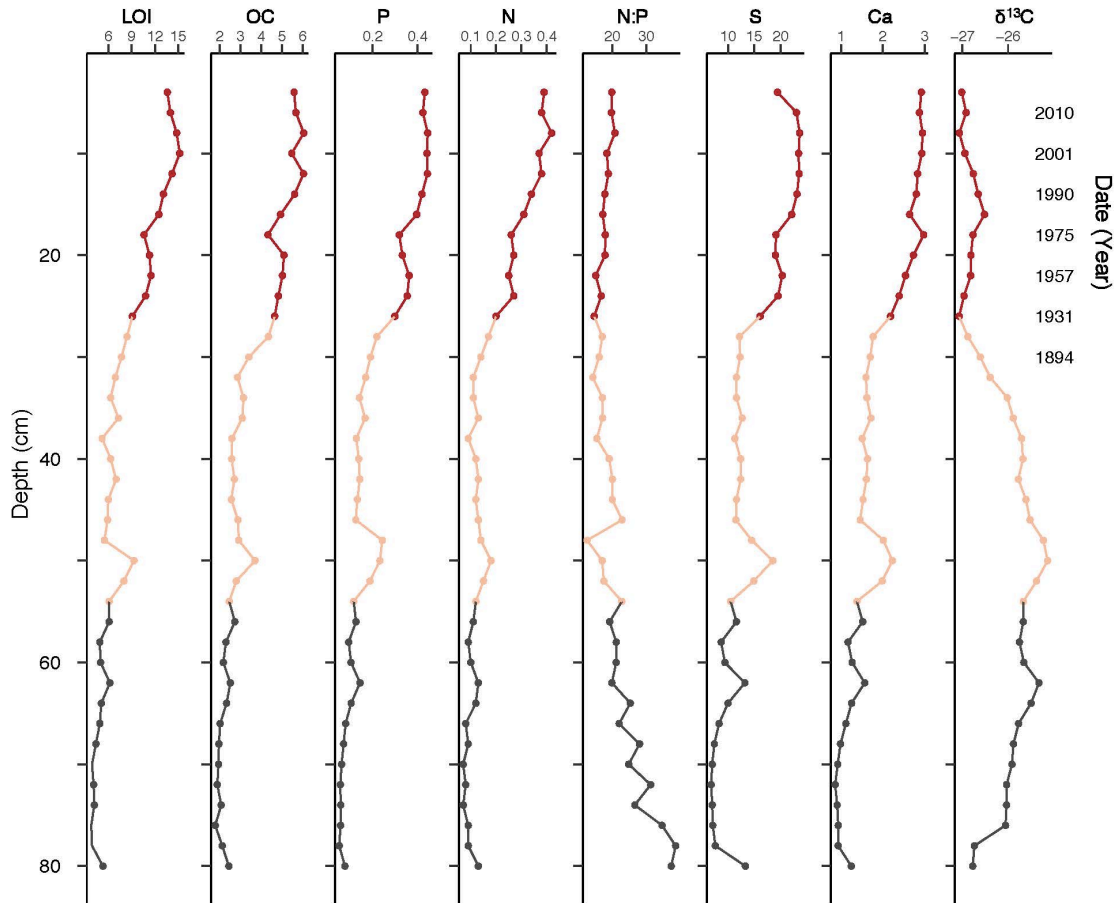


Figure 2.7. Core profiles of inputs for PB12. Loss on ignition (LOI), organic carbon (OC), and nitrogen (N) reported in percent. N:P is expressed in a molar ratio. Phosphorus (P) and sulfur (S) measured in mg g^{-1} . $\delta^{13}\text{C}$ expressed in ‰. Each color signifies a different cluster determined via k-means cluster analysis.

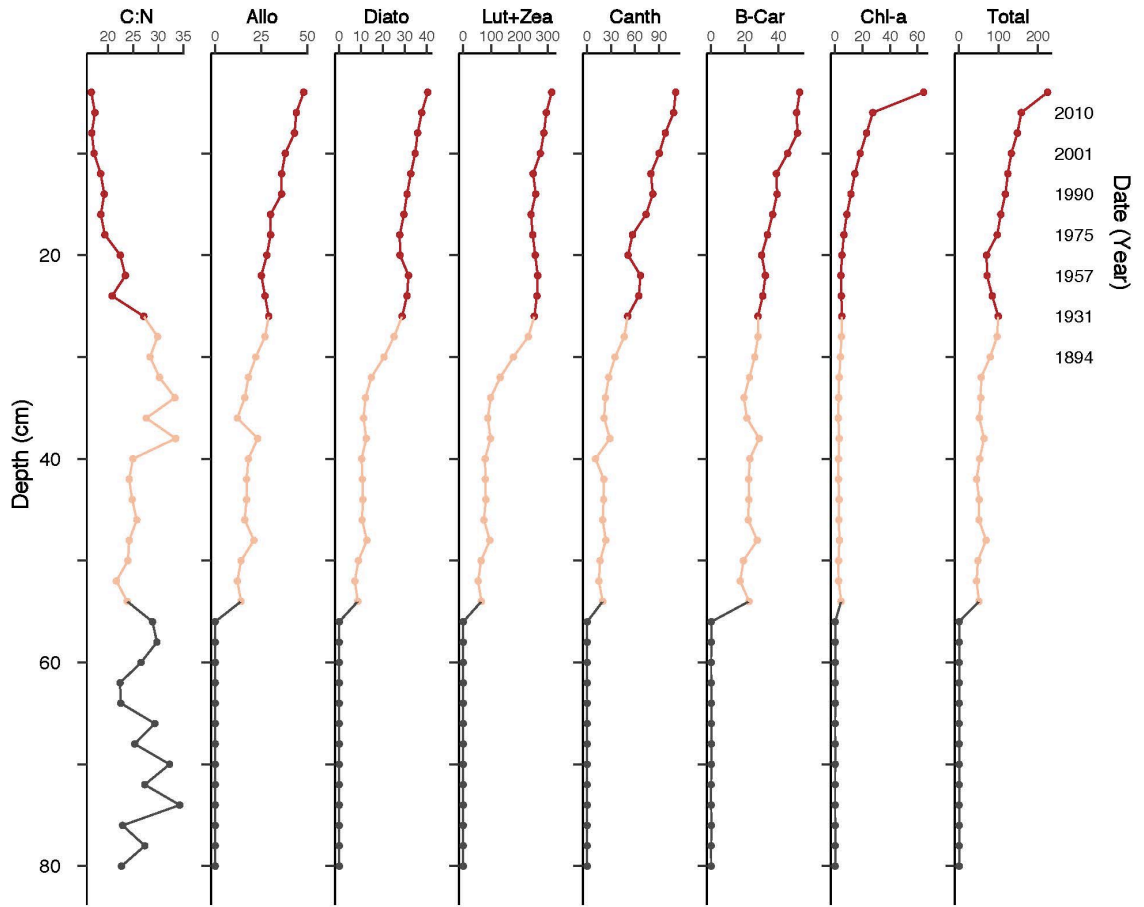


Figure 2.8. Core profiles of biologic variables for PB12; variables represent biological responses to increased nutrient inputs. Carbon-nitrogen ratios (C:N) expressed as a molar ratio. Photosynthetic pigments (Allo, Diato, Lut+Zea, Canth, B-car, Chl-a) measured in nmol/g organic matter.

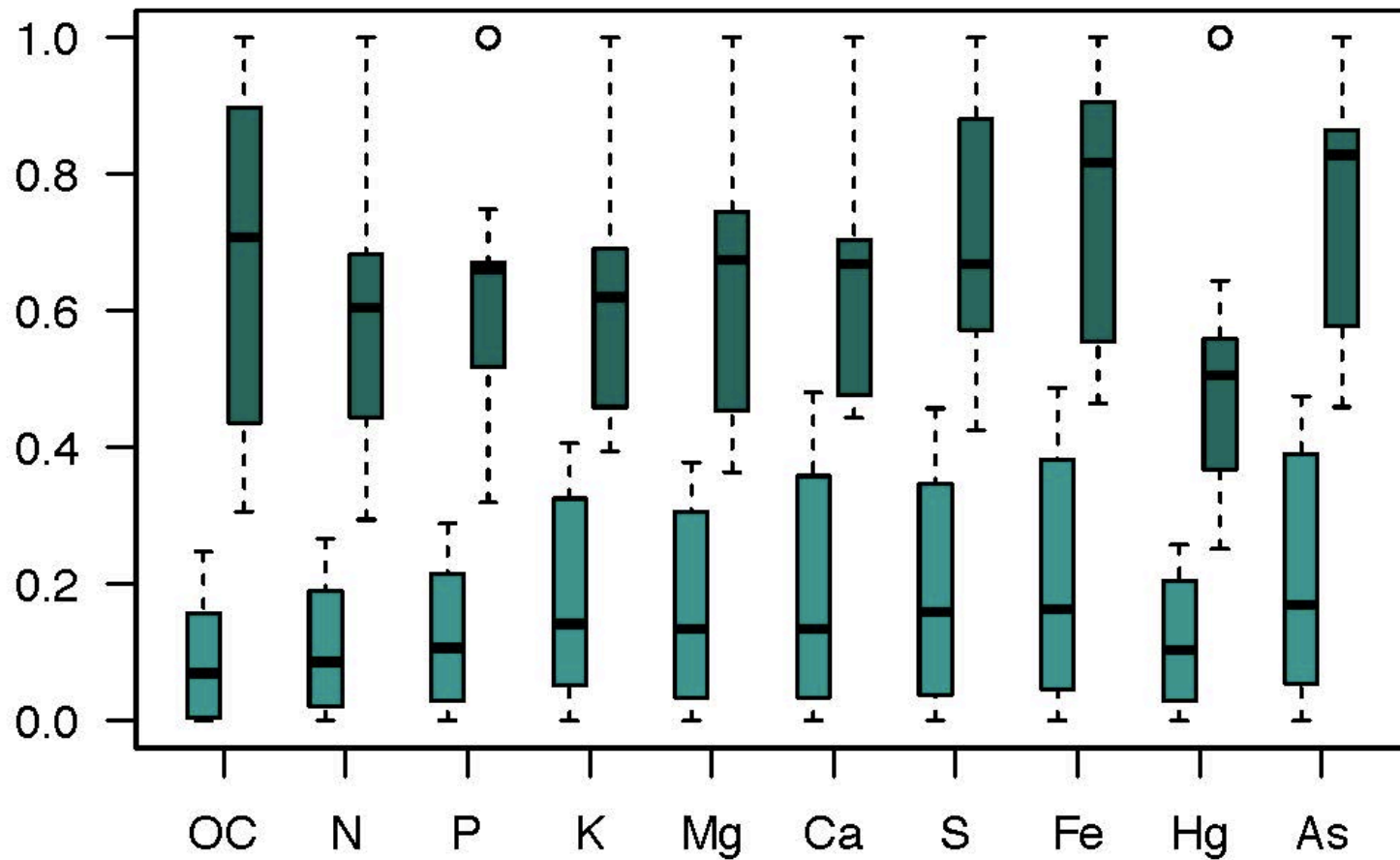


Figure 2.9. Box and whisker plot of normalized storage rates for selected analytes in WB1. Reference data were calculated in $\text{g m}^{-2} \text{yr}^{-1}$. Darker color signifies Cluster 1 (1978-2017) and lighter color signifies Cluster 2 (1927-1977).

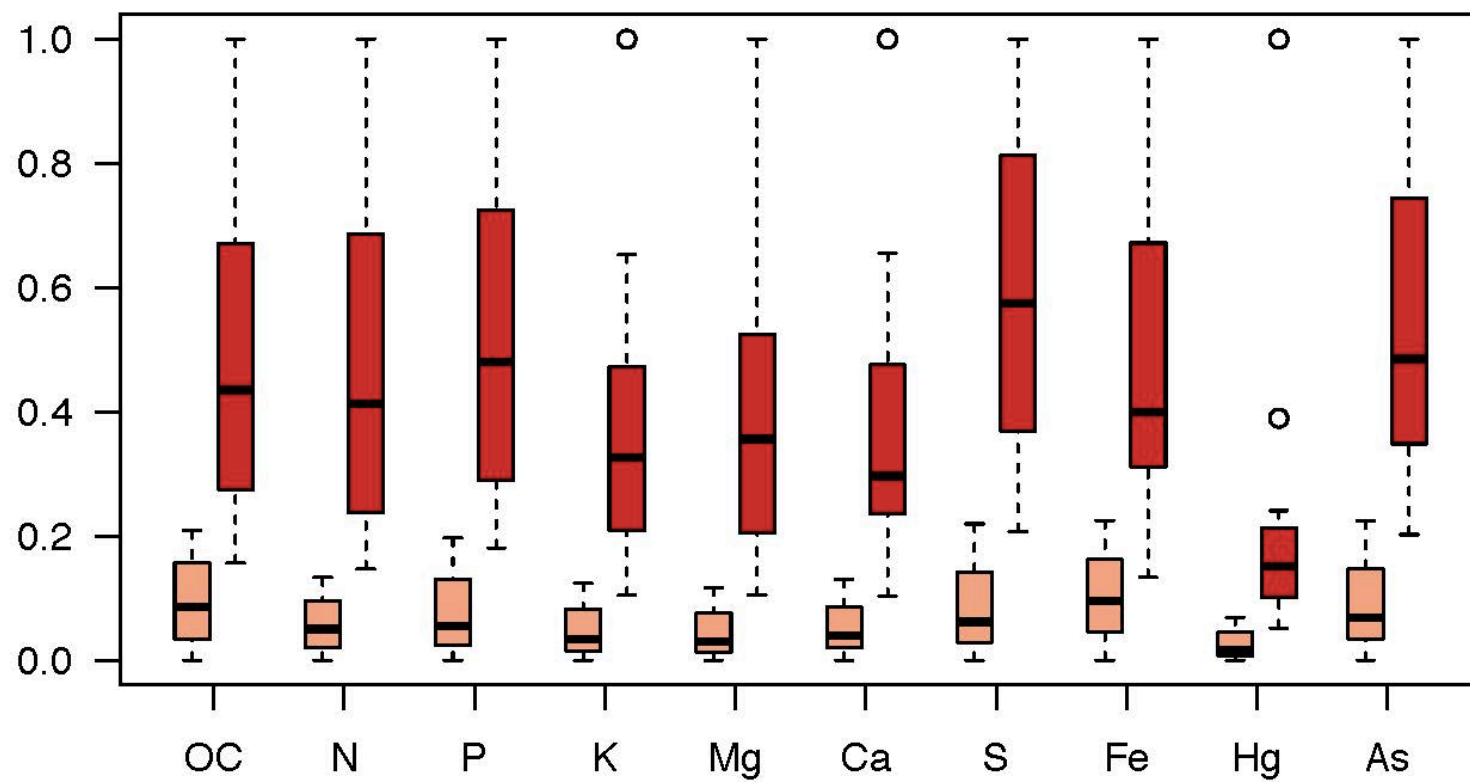


Figure 2.10. Box and whisker plot of normalized storage rates for selected analytes in PB12. Reference data were calculated in $\text{g m}^{-2} \text{yr}^{-1}$. Darker color signifies Cluster A (1939-2017) and lighter color signifies Cluster B (1864-1938).

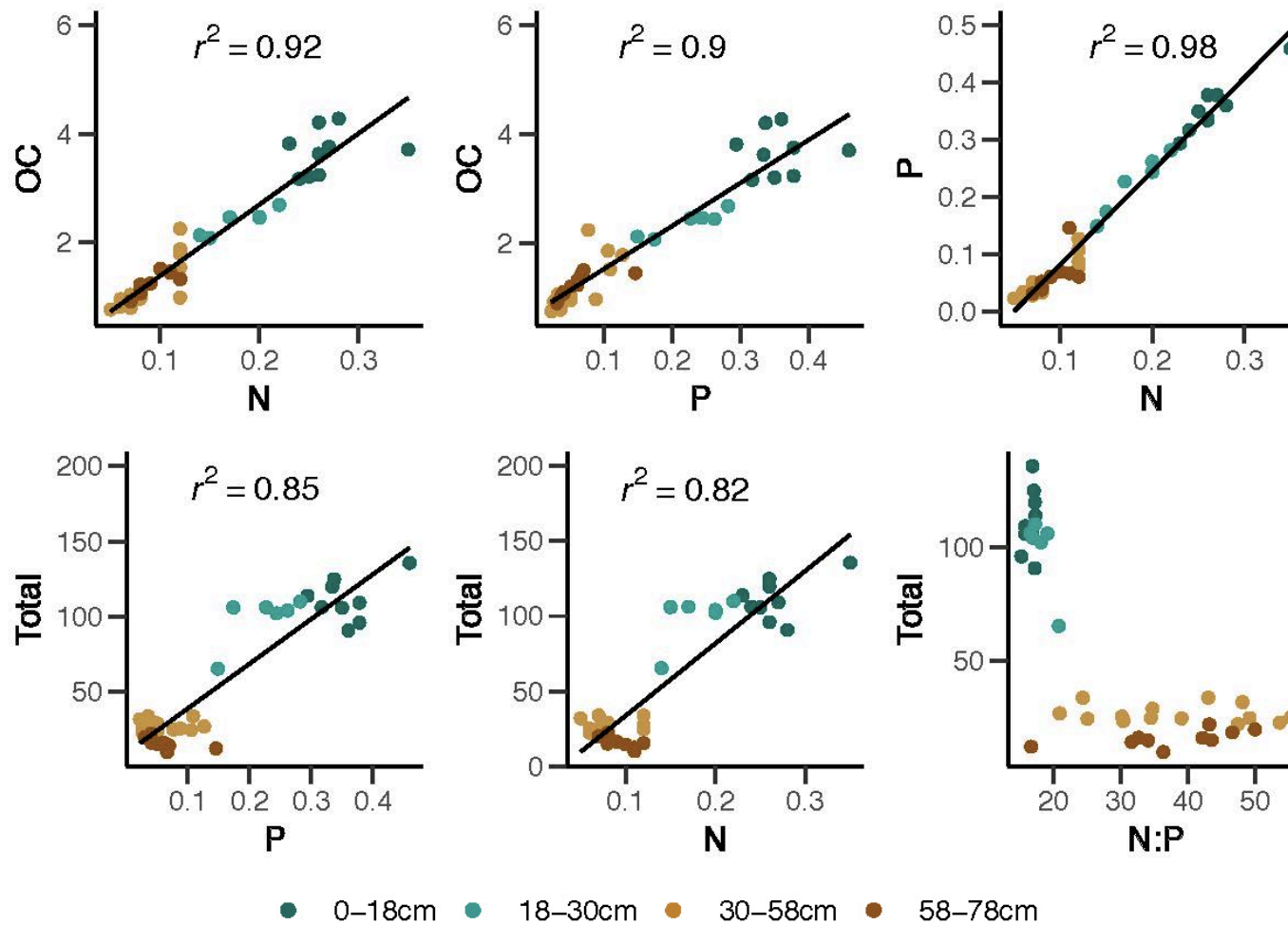


Figure 2.11. Scatterplots of correlations between nutrients (N, P) and primary producer indicators (OC, Total) for WB1. Correlation coefficients are expressed as r^2 values. Colors correspond to cluster determined by k-means cluster analysis.

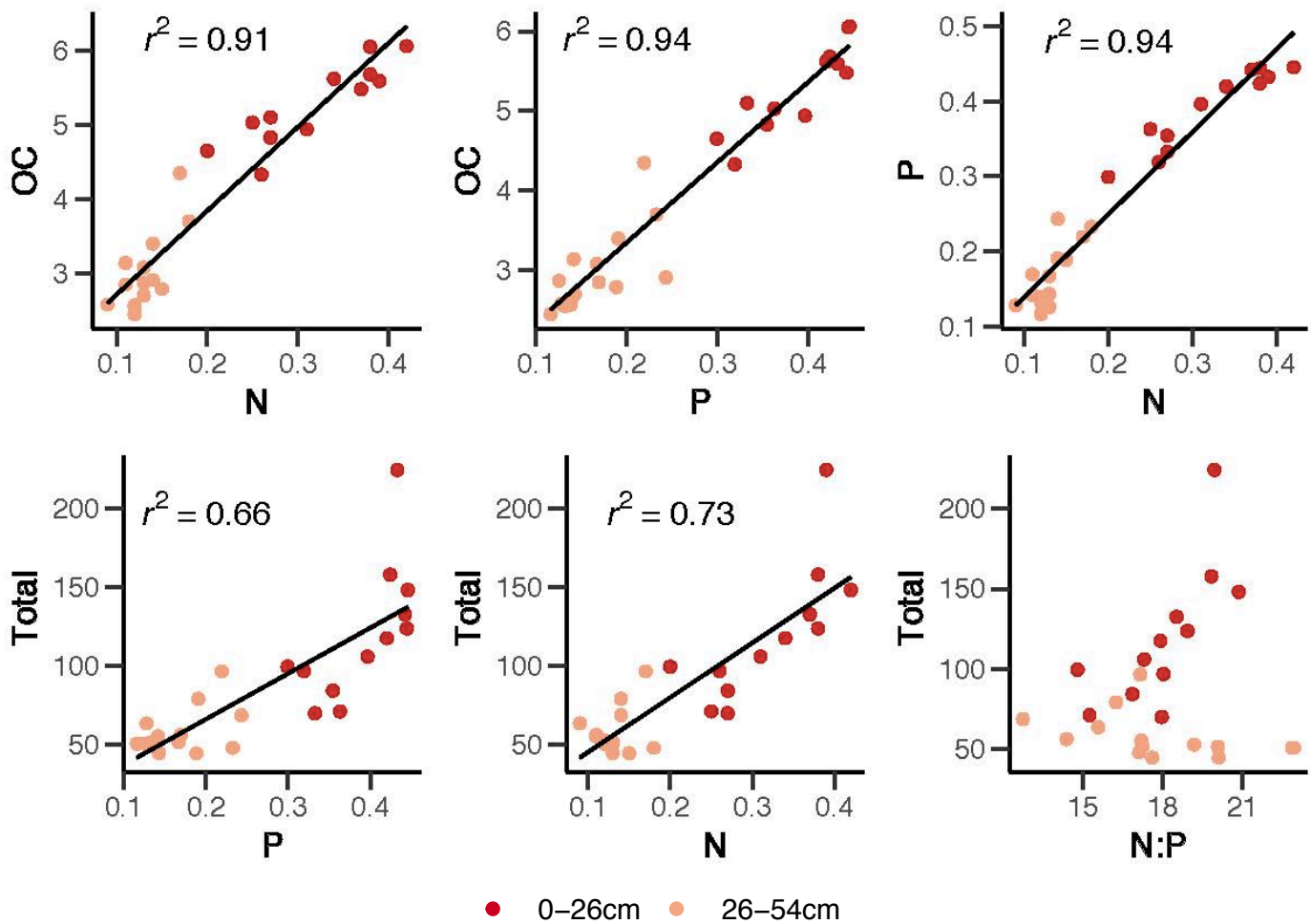


Figure 2.12. Scatterplots of correlations between nutrients (N, P) and primary producer indicators (OC, Total) for PB12. Correlation coefficients are expressed as r^2 values. Darker color signifies Cluster A (1939-2017) and lighter color signifies Cluster B (1864-1938).

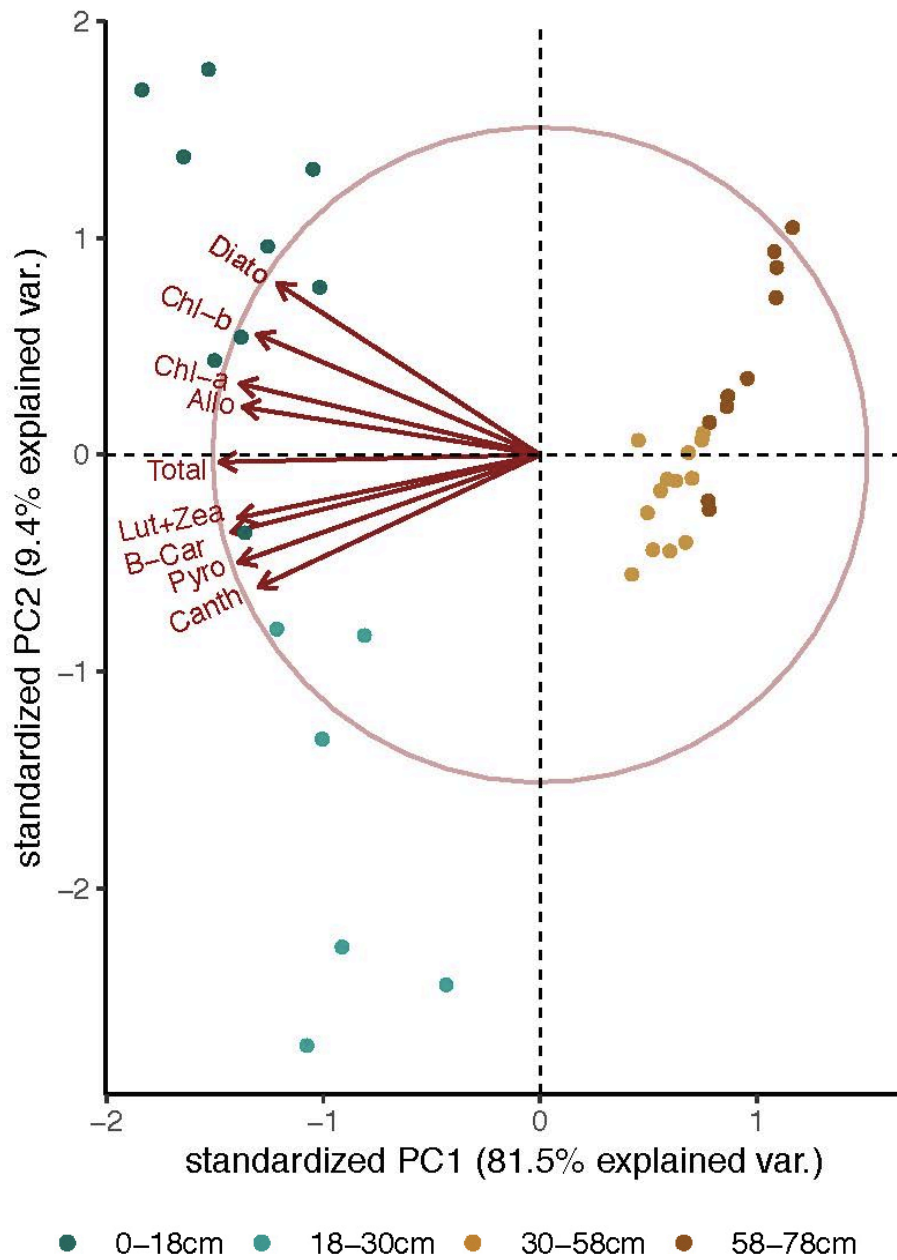


Figure 2.13. Biplot of principal components 1 and 2 of WB1 pigment data. Combined, principal components explain 90.9% of the variance in the pigment dataset for WB1. Color selection corresponds to cluster determined via k-means cluster analysis.

Chapter 3: Spatial Heterogeneity of Sediment Characteristics in a Gulf of Mexico Estuary System

Abstract: Coastal estuaries are complex and dynamic environments that provide an array of goods and services to humans but are declining due to increased anthropogenic pressure. In this study, surface sediment measurements of nutrients, photosynthetic pigments, and heavy metals were analyzed using a GIS software to determine the effect of anthropogenic impacts, explore relationships between nutrient inputs and phytoplankton dynamics, and identify potential sites of toxicity in a Gulf of Mexico estuary. Results indicate that nutrient loading appears to be linked to local land use while river discharge is a significant driver of phytoplankton community structure and abundance throughout the estuary. Additionally, high total chlorophylls suggest marine phytoplankton near marine inputs appear to be responsible for most of the primary producer abundance throughout the estuary. A possible link between urbanized areas and heavy metal pollution was also identified although no probable toxic sites, based on coastal Florida sediment quality guidelines, were identified in the study area. Analysis of the spatial relationships between these variables can lead to greater understanding of the drivers of estuary degradation in site-specific estuaries which should be applied in management and conservation efforts.

Introduction

Coastal estuaries are important ecosystems providing a variety of ecosystem services such as water filtration, sediment anchoring, and habitat for commercial and recreationally harvested species (Barbier et al. 2011). These dynamic ecosystems are influenced by a multitude of natural and anthropogenic factors including freshwater inflow, tidal action, nutrient pollution, hydrologic alterations, and climate change impacts. Classification as an estuary requires a coastal body of water to experience tidal action, maintain connection with a sea or other large marine water body, and receive freshwater input that results in significant dilution of sea water (Perillo 1995). The interaction of freshwater inflow and tidal action affects many biogeochemical properties of estuaries including nutrient dynamics (Nowicki and Oviatt 1990), phytoplankton community structure and productivity (Dorado et al. 2015), and heavy metal storage and mobility (Du Laing et al. 2008). Furthermore, the effects of anthropogenic influence have become increasingly significant as increasing global populations alter land for agricultural production, urbanize coastal areas, and impact and amplify climate dynamics (Doney 2010).

Nutrient loading predominantly from agricultural practices and wastewater-treatment-plant effluent has negatively impacted estuaries resulting in eutrophication (R. W. Howarth 1984). Eutrophication is an increase of phytoplankton in the water column and has many negative impacts such as decreased water quality, hypoxia, toxin production, loss of coastal wetland species, and harmful algal blooms (R. W. Howarth 1984; Sellner et al. 2003; Nyström et al. 2012). In addition to eutrophication, heavy metal pollution from industrial runoff, stormwater runoff, and atmospheric deposition from the

burning of fossil fuels has produced toxic conditions for biota in many estuaries (de Souza Machado et al. 2016). High concentrations of heavy metals in sediments can lead to lethal or sublethal (growth inhibition, morphological and behavioral changes) effects in estuarine organisms (Bryan and Cole 1971). Bioaccumulation of heavy metals further increases toxicity as trophic level increases and poses a risk to humans as many seafood species spend time in estuaries at some point in their life cycle (Guthrie et al. 1979).

Multiple investigations have modeled and compared the spatial distribution of specific variables related to anthropogenic impacts within estuary systems. Boyle et al. (2004) compared spatial variations in the water column and sediment nutrients to determine the seasonal availability of nutrients for phytoplankton. Dorado et al. (2015) noted the spatial partitioning of phytoplankton communities along an estuary gradient of varying salinity by identifying phytoplankton directly from the water column. Sin et al. (1999) studied nutrient and phytoplankton trends by comparing nitrogen, phosphorus, and chlorophyll-a concentrations within water samples along an estuary gradient and found river discharge to be a major controlling factor of phytoplankton biomass due to light limitation in the tidal-fresh water transition zone. Heavy metal concentrations have also been modeled to analyze the toxicity potential in sediments and identify sources and areas of concern (Caeiro et al. 2005; Birch and Olmos 2008). These studies collectively demonstrate that an understanding of spatial dynamics provides unique information concerning the integration of material inputs and ecological components of dynamic estuary systems. However, very few studies investigate the links between nutrient inputs and phytoplankton dynamics utilizing surface sediments which provide long term ecological insights that discontinuous water sampling cannot.

This purpose of this study is to apply surface sediment analysis throughout the Perdido Bay estuary system and examine estuary processes with an interdisciplinary approach utilizing surface sediment analyses to reflect multi-year trends as opposed to the highly variable (annually, seasonally, and daily) conditions captured by more traditional water column samples. Sediment samples were collected from ~60 sites throughout Perdido Bay and Wolf Bay, Alabama, USA to analyze spatial trends of nutrient, phytoplankton, and heavy metal deposition using geospatial techniques in an effort to increase understanding of estuarine sediment dynamics in the face of anthropogenic influences. The primary objectives of this study were to (1) link nutrient (N, P) inputs and distribution with terrestrial sources, (2) determine the drivers of the phytoplankton community structure and abundance along the estuary gradient and (3) identify the sources and sediment distribution of heavy metal pollution in addition to areas of potential heavy metal toxicity.

Methods

Study Site

The Perdido Bay system is comprised of two primary bays, Perdido Bay and Wolf Bay, which are located in the coastal area along the border of Alabama and Florida, USA. Perdido Bay feeds into the Gulf of Mexico and is approximately 130 km² with a watershed of 3,238 km² (Fig. 3.1). The primary tributary of Perdido Bay is the Perdido River, but 11 Mile Creek, Bayou Marcus Creek, and the Styx and Blackwater Rivers are also significant sources of freshwater inflow. Wolf Bay is a sub-estuary of Perdido Bay and is located between Mobile Bay to the west and Perdido Bay to the east. Wolf Bay

covers an area of about 126 km², and receives inputs from Perdido Bay and also Mobile Bay via the Gulf Intracoastal Waterway which was created in the early 1930s (Alperin 1983). Water levels for both bays are largely determined by freshwater inflow as the diurnal tidal range is small (<.5 m) throughout the system (Schropp 1991; Macauley et al. 1995).

These estuaries exist on the border of Baldwin County, Alabama and Escambia County, Florida. Both counties have experienced rapid urbanization and the combined population of the two counties has more than tripled since 1950. Bordering towns of Pensacola, Orange Beach, and Foley have all expanded rapidly due to recent population and urbanization increases. In addition to urban land use/land cover, land use in the area bordering lower Perdido Bay is predominately agricultural (Fig. 3.2). Human land use has negatively impacted water quality and ecosystem health for both Perdido and Wolf Bay (Wang and Kalin 2018) with eutrophication, hypoxia, and habitat loss all being documented as early as the 1960s (Altsman and DeMay 2007; World Resources Institute). The causes of ecosystem decline are debated, but primarily attributed to anthropogenic nutrient loading and climate change impacts such as sea level rise and increasing sea surface temperatures (R.J. Livingston 2014). Schropp et al. (1991) found evidence of anthropogenic nutrient loading in each of Perdido Bays' primary tributaries in addition to evidence of heavy metal contamination from urban runoff. Livingston et al. (2007) studied phytoplankton communities and found inputs from paper plant effluent in 11 Mile Creek to be a primary driver of eutrophication in the upper bay, while agricultural runoff appeared to have greater effect on the lower bay.

Site Selection & Sample Collection

Sample sites were selected to spatially represent the entire bay system as well as each major stream or marine input throughout the basin (Fig. 3.1). Samples were collected ~1.5 kilometers from the nearest sample site and density was adjusted slightly according to basin size. Care was taken to avoid sampling close to the shorelines to circumvent collecting sediment that was not representative of each estuary basin. Sediment samples were collected using a ponar dredge and homogenized in a large container before a sub sample was removed and stored in polyethylene sampling bags to reduce risk of contamination. Samples were then stored on ice and transported to the Auburn Paleoenvironmental Lab. Upon arrival, a 4.93cm³ aliquot was removed for loss-on-ignition (LOI) analysis, and about half of the remaining sample was removed and frozen to serve as an archive. The remainder of the sample was frozen, lyophilized, ground to a homogenous powder, and stored in a freezer to ensure consistency of further analyses.

Sediment Analyses

LOI was calculated by comparing mass of a known volume (4.93 cm³) of lyophilized sediment in pre-weighed crucibles before and after burning in a 550°C muffle furnace for three hours to volatilize organic matter (Hakanson and Jansson 2011). Total carbon (TC) and nitrogen (N) were measured using a in a Costech combustion elemental analyzer with an attached autosampler. Phosphorus and heavy metal (Zn, Cu, Cr, Pb, Cd, Ni) concentrations were measured using an ARL 3560AES ICP analyzer following acid digestion in a heated block using EPA method 6010B at Waters Agricultural Laboratories

(watersag.com). Heavy metal toxicity potential was determined using the sediment quality guidelines (SQG) for coastal Florida (Dyer 1995). Mean sediment quality guideline quotients (mSQGQs) were calculated to determine the combined potential of toxic conditions from measured heavy metals at each site (Long 2006).

Photosynthetic pigment (chlorophylls and carotenoids) concentrations were measured using High Performance Liquid Chromatography (HPLC) following the methods of Waters et al. (2015) and Leavitt and Hodgson (2001). Sediment samples were weighed in 2 mL microcentrifuge vials and extracted at -20°C for 16-20 hours in a solvent composed of acetone, methanol, and water at a ratio of 80:15:5. Samples were then centrifuged and filtered through a 0.22 µm syringe filter to remove particulate matter and placed in the autosampler of a Shimadzu HPLC system. The autosampler then mixed samples with an ion-pairing agent at a 3:1 ratio and injected the mixture into the HPLC following the phase and time sequence of Leavitt and Hodgson (2001). Photopigments were separated using a Phenomenex Luna C18 column and chlorophylls were measured by a fluorescence detector while carotenoids were measured by a photodiode array detector. Pigments were then identified by retention times and spectra of standards and expressed as nmol per gram organic matter.

Spatial Analyses

ESRI's ArcGIS Pro 2.3.1 was utilized to conduct a suite of spatial analysis tests and techniques. The kernel interpolation with barriers tool within the ESRI geostatistical wizard was utilized to convert point data from sample sites into continuous data to visualize trends of multiple variables (C:N, TC, LOI, P, N, Total, Fuco, Chl-x, Canth,

Zea+ Lut, Allo, and mSQGQ), and the application of barriers was vital in properly modeling variables throughout the irregular shape of the study system by properly weighting samples that were separated by dry land. The kernel interpolation with barriers tool is recommended for interpolating water quality data within estuaries and bays by ESRI and provided the best results statistically as evidenced by the lowest calculated root-mean-square-error (RMSE) between different interpolation strategies when cross validation was applied. The eye test was also used to throw out any interpolation visualizations that seemed impossible, unlikely, or poor representations of actual conditions. The chosen interpolation models were then optimized by adjusting bandwidths to create the lowest RMSE and replicate observed and predicted data distributions as well as possible.

The hot spot analysis tool within the ESRI spatial statistics toolbox was used to identify clusters of significantly high and low values for nutrient variables (P, N, TC) within the system. Exploratory OLS regression was also applied to explore the relationship between organic matter (LOI) and mSQGQ, but geographically weighted regression (GWR) proved more useful for further analysis due to the nonstationarity of the variables as indicated by p value of the Koenker (BP) Statistic from the OLS regression and provided better understanding of the regional variation present between exploratory variables. Univariate Moran's I was then utilized to ensure autocorrelation of residuals was not present.

Results & Discussion

Nutrient Inputs and Distribution

The direct input of terrestrial material by the Perdido River is demonstrated by the distribution of C:N values (Figure 3.3). Higher values are observed near most stream inputs, but a plume of the highest values (>15) originates near the Perdido River and extends throughout the upper bay denoting that terrestrial and recalcitrant inputs are a major component of sediments in the upper bay (Meyers and Teranes 2002). Low C:N values near Perdido Pass and the GIWW illustrate the increased deposition of algal detritus in the lower bays of both Perdido and Wolf Bay and marine inputs from the Gulf of Mexico and Mobile Bay. Acknowledging the primary origin of inputs (terrestrial vs. algal-freshwater vs. algal-marine) throughout the study area is necessary to make any further assumptions about the drivers and sources of nutrient deposition and storage as demonstrated by Bianchi and Argyrou (1997).

Sediment TC concentration (Figure 3.4) is lowest near Perdido River and Perdido Pass, and high in in the southeast side of upper Perdido Bay and the northwest side of lower Perdido Bay. The spatial distribution of TC is affected by a variety of factors including deposition of organic matter, proximity to the primary channel of water flow, local land use, or a combination of these factors. The interpolation of LOI values (Fig. 3.5) indicates organic matter composition is a driving factor of sediment carbon concentration and aligns with findings that a majority of carbon deposited is organic (88% in sampled locations). The distribution of TC and LOI values in upper Perdido Bay are likely due to influences of the Perdido River. High water velocity near the river mouth explains the low values calculated near Perdido River due to the sedimentation

properties of high-energy areas which typically result in organic matter-poor sandy sediments (Dyer 1995). The high values calculated in the southeast portion of the upper bay can thus be attributed to being out of the major channel of water flow, but are likely also influenced by increased algal productivity in the area as suggested by the C:N interpolation. One possible explanation for increased phytoplankton abundance is decreasing light attenuation further from the river mouth as dissolved organic carbon in the water column decreases (Cloern 1987).

The influence of the two most common limiting nutrients for primary productivity in aquatic habitats, P and N (Hans W. Paerl 2009), appear correlated with the distribution of sediment C concentrations. Both (Fig. 3.6 and Fig. 3.7) show similar trends to TC interpolations, but high values are more heavily observed throughout lower Perdido Bay in both instances. Hot spot analysis of P (Fig. 3.8) identifies sample points within the northern half of lower Perdido Bay as hot spots, and hot spot analysis of N (Fig. 3.9) identifies the entire lower Perdido Bay as a hot spot, and all of Wolf Bay as a cold spot with >90% confidence. Upper Perdido Bay contains no hot or cold spots for either nutrient which can be explained by the influence of the Perdido River for the same reasons as TC. Lower Perdido being identified a hot spot for P and N is likely due to land use in the surrounding area. The interpolation models predict the highest values along the northern shoreline of the lower bay where most of the agricultural land use in the watershed is concentrated. In addition, a wastewater treatment plant is located in the same area and has experienced collection system failure multiple times in the past, most recently in 2012 (ADEM). While these areas along the border of the interpolation have the highest standard error, the model does take into account the trends of all other data

points, and therefore the shoreline should be considered a major source of nutrient pollution for this system though values may not be as extreme as predicted. However, hot spot analysis of TC (Fig. 3.10) identifies upper Perdido Bay as a hot spot and Wolf Bay as a cold spot, which is an indication that nutrient concentrations may not reflect organic matter deposition across the gradient of the river-estuary-interface. This suggests interactions between river discharge and tidal action influence carbon sedimentation processes more than nutrient pollution.

The importance of tidal action has been previously documented in other estuaries with Allen et al. (1980) noting the exportation of sediments in macrotidal (4-7m) estuaries. The Perdido Bay system experiences microtidal action (.2-.5m) which appears to encourage sedimentation in lower Perdido Bay but reduce sedimentation of organic matter in the channels that connect Perdido Bay to Perdido Pass. Furthermore, Gong et al. (2014) analyzed the patterns of sedimentation in a microtidal, funnel-shaped estuary with a primary channel and found fine particulate matter to travel seaward in the primary channel, but landward in the shallower shoals on either side of the channel. Though the Perdido Bay system is a morphologically different estuary with less connectivity to the ocean, this study suggests that the general patterns of sedimentation are similar with significant outwelling in primary channels and more sedimentation in shallower, non-channelized areas of the bay. These findings demonstrate the multiplicity of factors that drive sedimentation of nutrients throughout an estuary, but also highlight the possibility of combining these techniques to identify pollution sources.

Primary Producer Abundance and Community Distribution

Interpolation of Total Chlorophylls (Fig. 3.11) shows the highest concentrations were located near saline inputs, namely Perdido Pass, Wolf Bay's connection to the GIWW, and Bayou Garcon. The first two areas receive inputs from the Gulf of Mexico and Mobile Bay, and Bayou Garcon is primarily composed of an intertidal salt marsh that does not experience most of the flushing pressure from Perdido River like the rest of the bay. These findings are unexpected because they imply that primary producer abundance is not highly correlated with nutrient concentrations but is instead driven by conditions found in more marine and saline environments. While salinity is an evident explanation for the observed distribution of Total Chlorophyll, many species of phytoplankton exist throughout an estuary gradient that can compete and flourish in varying saline conditions (Ferreira et al. 2005; Muylaert et al. 2009). It is more likely that a combination of factors influences these observations. High levels of light-limiting dissolved organic carbon from freshwater inflows likely limits primary productivity in fresher areas of the system (Harding et al. 1986). Higher flushing forces near streams in the upper portions of each bay could also decrease deposition of nonmotile algal detritus, but the inverse Total-Chl correlation with C:N discredits that connection. In addition, the locations with the highest observed and predicted values are most heavily influenced by tidal action, implying greater connectivity with intertidal wetland habitat is another possible explanation (T. S. Bianchi and Argyrou 1997), but most of the intertidal habitat in the southern portion of Perdido Bay is developed with Bayou Garcon being the largest exception. Since total chlorophyll concentrations are weighted by organic matter, the high concentrations observed could also be an artifact of these calculations because LOI was very low in

sandy sediments where high Total values were measured. However, this concept more likely suggests that the organic matter that is deposited is rich in chlorophyll thus primarily algal (Wysocki et al. 2006). Tidal action offers another possible explanation of high concentrations of Total Chlorophylls southernmost channels of the system since tidal action is typically assumed responsible for outwelling of algae in macrotidal systems (Monbet 1992), but Perdido Bay experiences very little tidal action, particularly near Perdido Pass (.2m) where high values were measured. Further analysis of the spatial distribution of community specific photopigments offers insight on determining the local drivers of phytoplankton abundance.

Photopigment distribution followed two general patterns. Fucoxanthin (Fig. 3.12) and an unknown chlorophyll believed to be divinyl chlorophyll-a (Chl-x) (Fig. 3.13) were observed in high concentrations in the same general locations as Total Chlorophylls. In an ecological study of Perdido Bay, epiphytic diatoms and brown algae were observed in large quantities in nutrient enriched seagrass beds, and fucoxanthin is a primary indicator for these communities and was found to explain 88% of the variance in Chl-a (Wear et al. 1999). The highest Fuco values observed in this study were located nearest Perdido Pass, where most of the area's seagrass meadows and sandy sediments are located (FDEP), and near the GIWW input to Wolf Bay which also has a small seagrass meadow as confirmed by satellite imagery. These factors indicate that seagrass meadows provide vital habitat that contribute to a large portion of the phytoplankton abundance for the entire system (Moncreiff and Sullivan 2001). Additionally, the strongest explanation for high chlorophyll and fucoxanthin values in the sandy sediments near Perdido Pass is the presence of epipsammic diatoms- benthic, sand-dwelling algae that thrive in clear water

conditions (Wetzel 2001). Epipsammic diatoms in collected surface sediment samples would reflect living algal presence rather than detritus as evidenced by the lack of apparent connection with sedimentation and could create positive bias of Fucoxanthin and Total-Chlorophyll measurements near Perdido Pass. The interpolation of Chl-x displays a similar pattern to Fuco except with much higher concentrations near Bayou Garcon. This chlorophyll was not explicitly identifiable but was observed in high concentrations near major saline inputs and assumedly represents another specialized phytoplankton community that thrives in saline conditions.

Conversely, the highest concentrations of Canth, Zea+Lut, and Allo were observed nearest major riverine inputs (Perdido River, Moccasin Bayou). Canth (Fig. 3.14) and Zea (Fig. 3.15) are both indicative of cyanobacteria, which are motile, uptake nutrients quickly, and fix nitrogen directly from the atmosphere (H. W. Paerl and Fulton 2006). These qualities allow cyanobacteria communities to thrive in the light-limited conditions of the upper bays and have been associated with high DOC in other studies (Waters et al. 2012; Cottingham et al. 2015). Cryptophytes, indicated by Allo concentrations (Fig. 3.16), can flourish in DOC-rich environments due to their ability to supplement their growth with DOC intake or ingestion of bacterial prey when conditions are not ideal for photosynthesis (Johnson et al. 2018). The distribution of cyanobacteria concentrations suggest that they are the dominant community throughout a large area of the bay, but it is also an area of significantly low productivity, so the negative impacts of these species seem to be naturally mitigated. Furthermore, these findings indicate that light limitation is a primary driver in phytoplankton community structure and abundance

and that anthropogenic nutrient loading may not be as important as freshwater inflow as a driver or inhibitor of eutrophication.

State of Heavy Metal Toxicity

Overall, sediment heavy metal concentrations followed similar depositional patterns as organic matter. Calculated mSQGQ values ($.43 \pm .3$) indicated combined heavy metal concentrations were not above the level of possible (TEL) or probable effects (PEL) at any locations. However, Cr (n=15), Pb (n=22), Cd (n=3), and Ni (n=1) were present in concentrations over TEL guidelines, but no metals were observed over PEL concentrations. Low mSQGQ values calculated near high-energy depositional zones and high mSQGQ values located in low-energy depositional basins (Fig. 17) indicate sediment toxicity is correlated with deposition of organic matter. This inference is further supported by the high correlation between mSQGQ and LOI (global $r^2=.63$) and the findings of Lin and Chen (1998). Spatially, local r^2 values (Fig. 18) were lowest near the Perdido River input ($\sim.5$), and highest in Wolf Bay and near Perdido Pass ($\sim.8$) demonstrating that a major riverine input significantly lessens predictivity of heavy metal concentration based on organic matter deposition. Furthermore, high mSQGQs were observed near subwatersheds that contained the cities of Foley and Pensacola suggest sediment heavy metal concentration is also influenced by urban inputs such as stormwater runoff and industrial effluent. Overall, heavy metal concentrations of observed sites in Perdido and Wolf Bay were below levels of possible or probable toxic conditions, but mSQGQs ($\sim.95$) were predicted near Perdido Beach and the northwest

branch of Wolf Bay indicating that these areas should be directly observed as a precautionary measure.

Conclusion

The spatial trends of deposited materials throughout Perdido Bay reflect the heterogeneity of environmental conditions experienced by estuary systems and associated biota (Thrush et al. 2008). While Perdido Bay experiences minimal tidal influence, other drivers were associated with different spatial areas of system. The upper Perdido Bay area contained sediments reflecting terrestrial inputs and appear to be governed largely by riverine inputs. Wolf Bay possesses significantly less riverine influence, which allowed for a variety of drivers impacting sediment deposition. Lower Perdido Bay appeared to be impacted by non-point source nutrient inputs from the north and marine algal inputs in the southern areas connected to the Gulf of Mexico. As a result, each area of the estuary experienced differing drivers of material deposition. Likewise, urban sources appear to be more localized to direct industrial inputs. The diverse spatial variability of biogeochemical factors and indicators measured throughout this study highlight the heterogeneity of estuaries and the complexity of anthropogenic influence.

The findings of this study align with the site-specific conclusions of Schropp (1991) and Livingston (2007), though this study is far more recent and utilized surface sediment analysis rather than water column analysis. Furthermore, the importance of hydrology, specifically freshwater inflow and tidal action, is emphasized far more in this study than the former, a finding which coincides with Sin et al (1999), a study that analyzed correlations between nutrients and phytoplankton in the water column. The

agreement between previous studies and the conclusions of this study indicate that spatial analysis of sediment variables can provide valuable insight of estuary processes because surface sediment samples are representative of longer time periods than daily water column grab samples or seasonal monitoring studies. Additionally, the findings of this study imply that care should be taken when altering estuary hydrology to avoid unintended impacts to local ecology and storage dynamics which are highly dependent on freshwater inflow and tidal action.

Figures

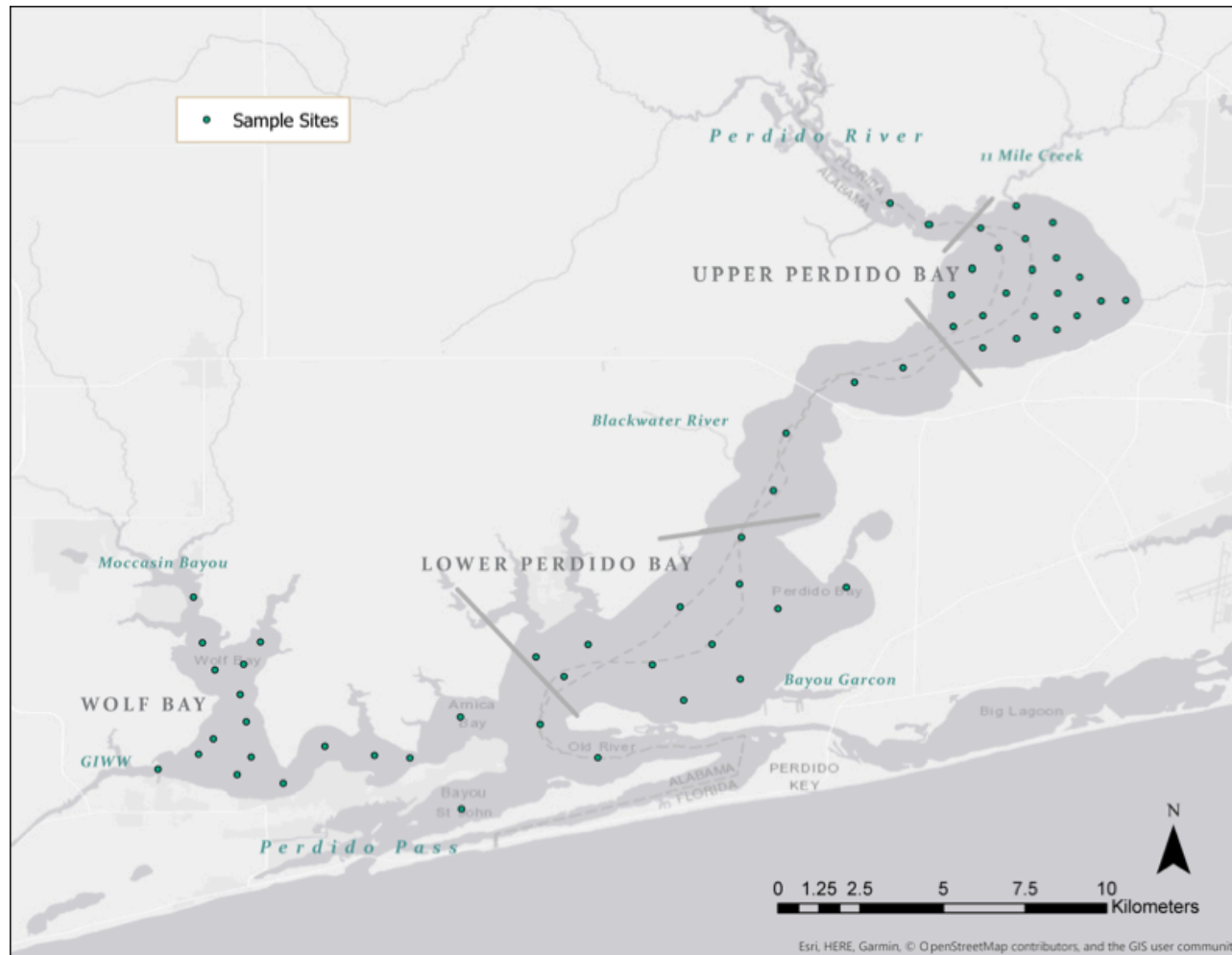


Figure 3.1. Map of Study Area. Mentioned locations are labeled accordingly. Points indicate surface sediment sampling sites.

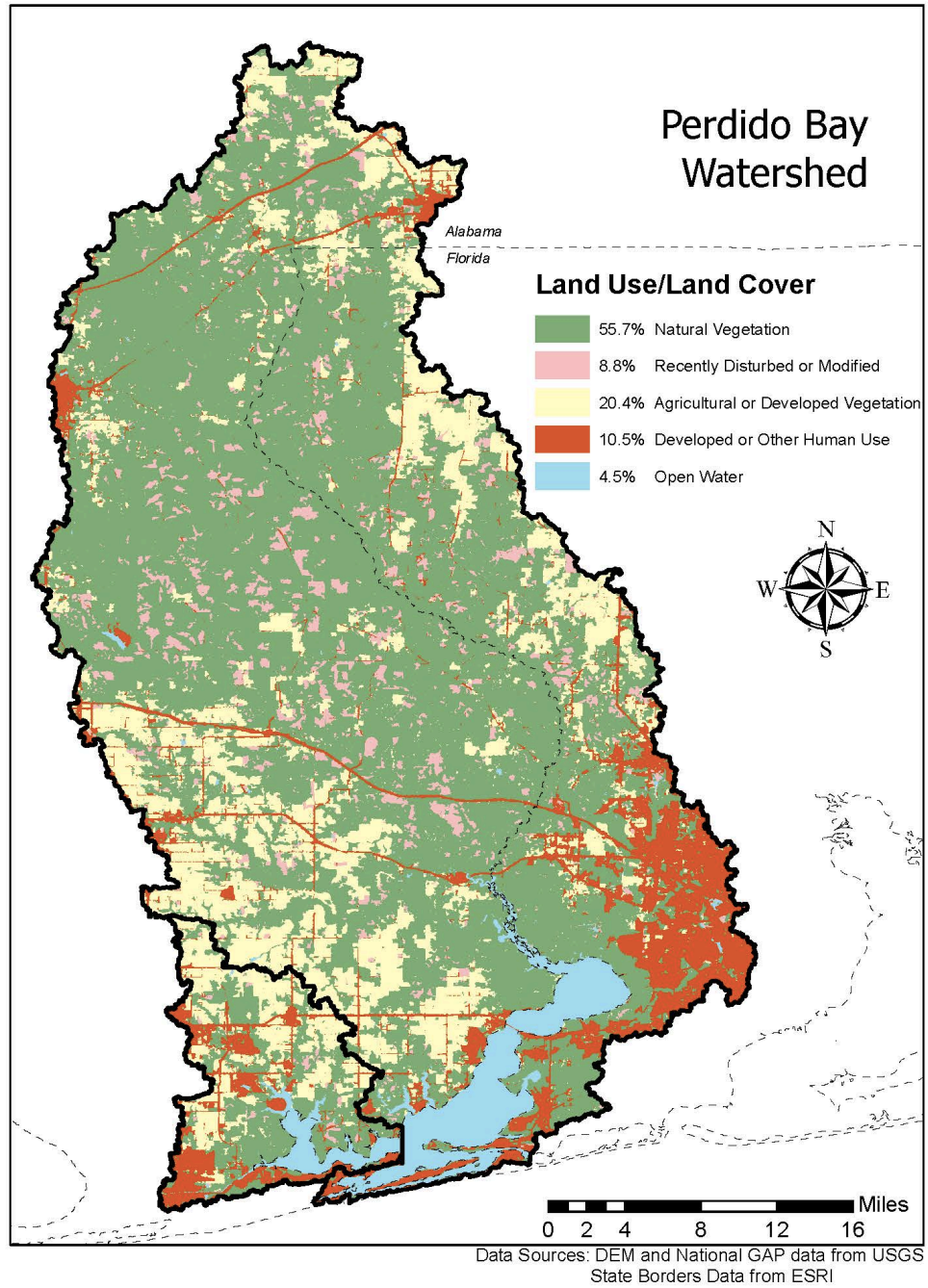


Figure 3.2. Watershed Land Use Map for Perdido Bay and Wolf Bay. The sub-watershed of Wolf Bay is indicated by the black outline within the Perdido Bay watershed.

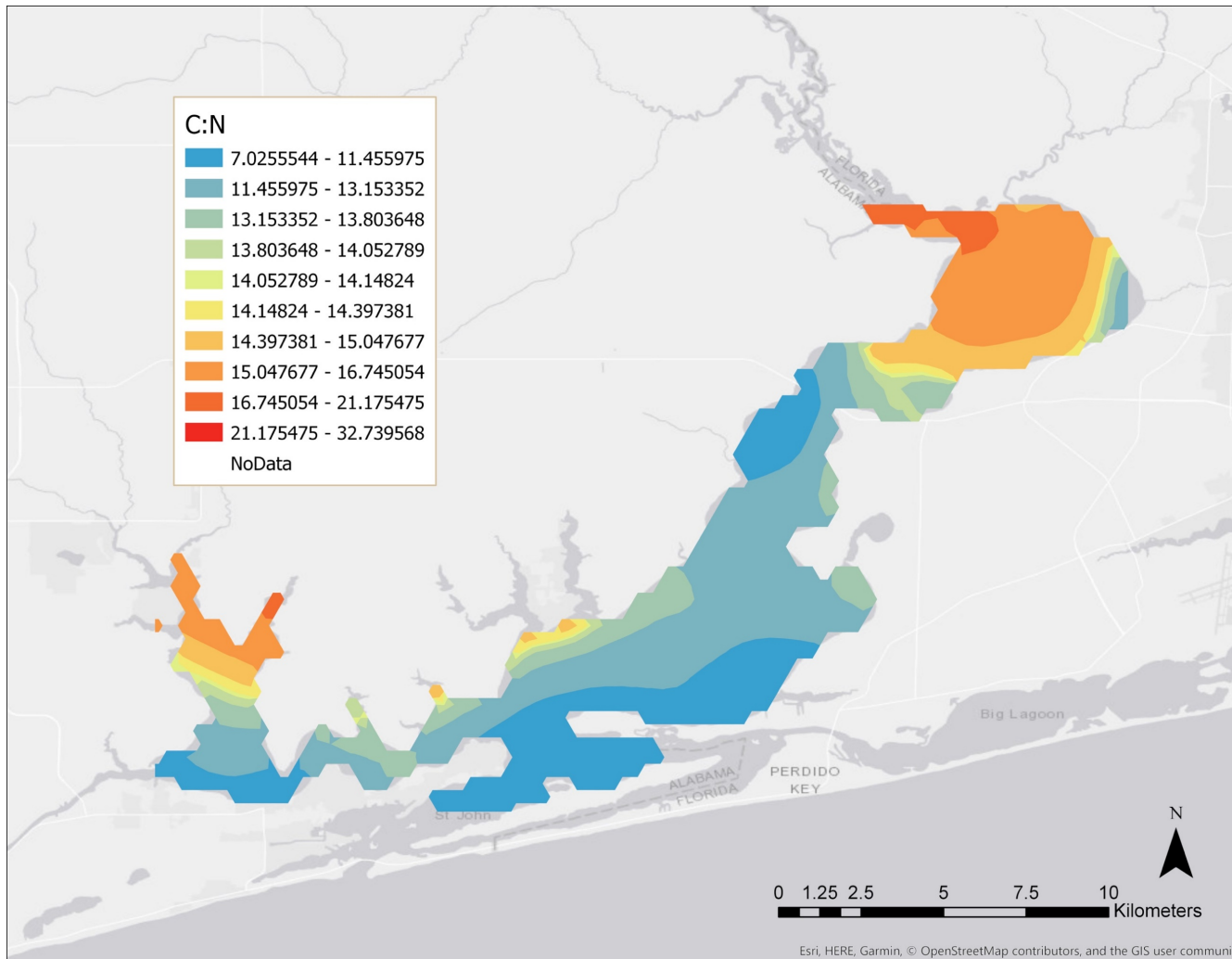


Figure 3.3. Interpolation of Sediment Carbon-Nitrogen Molar Ratios.

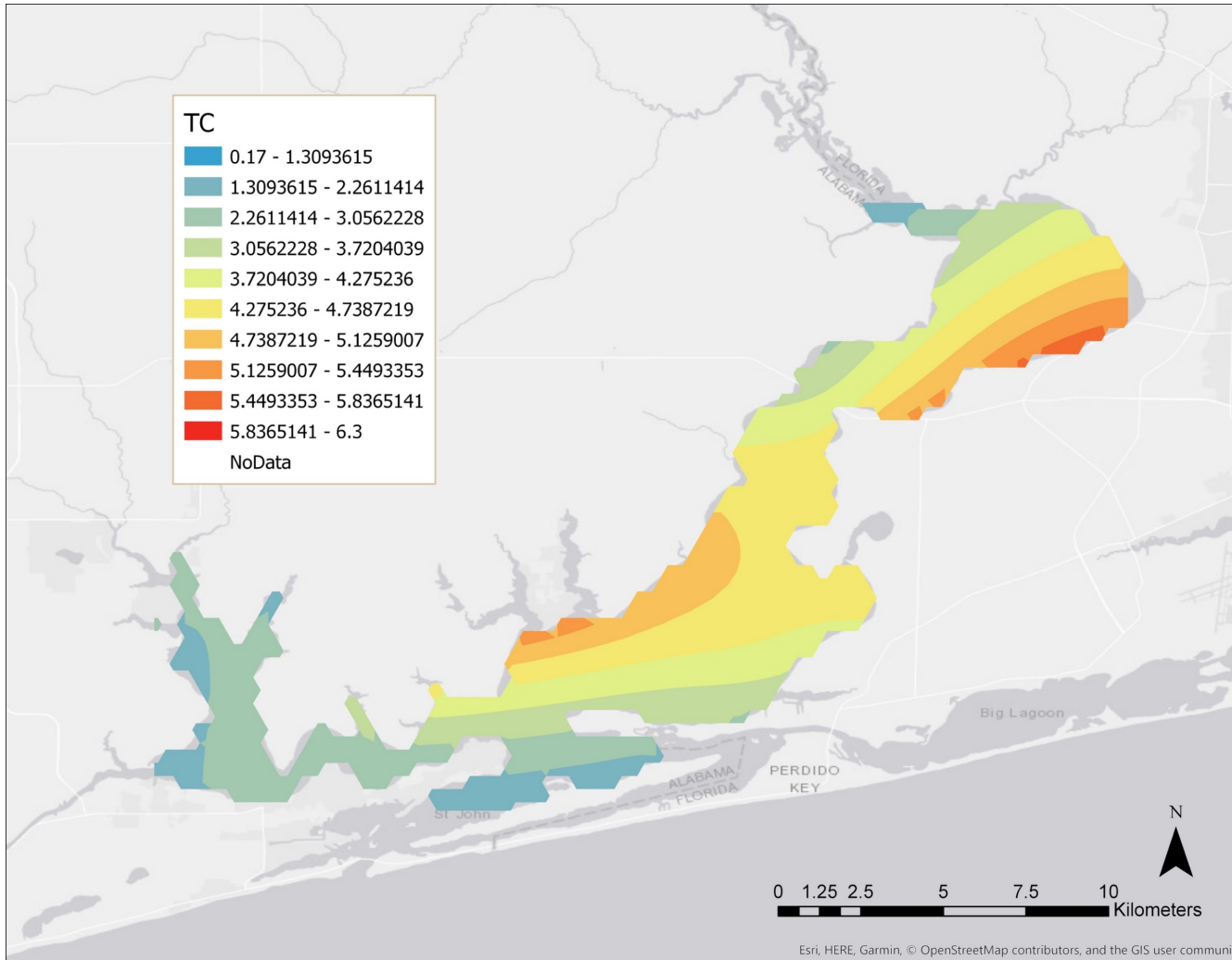


Figure 3.4. Interpolation of Sediment Total Carbon. Expressed as percentage (%).

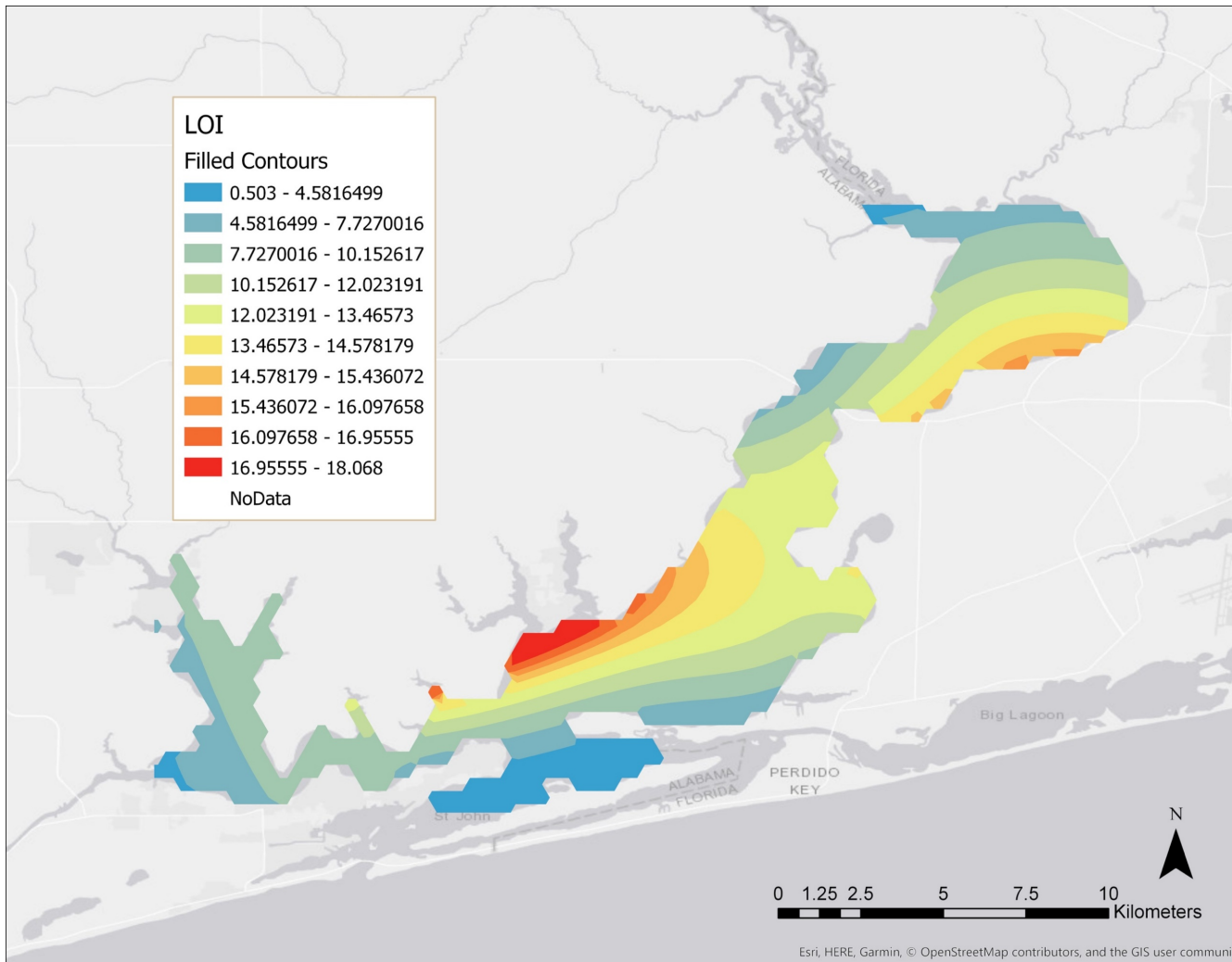


Figure 3.5. Interpolation of Sediment Loss-On-Ignition (LOI). Expressed as percentage (%).

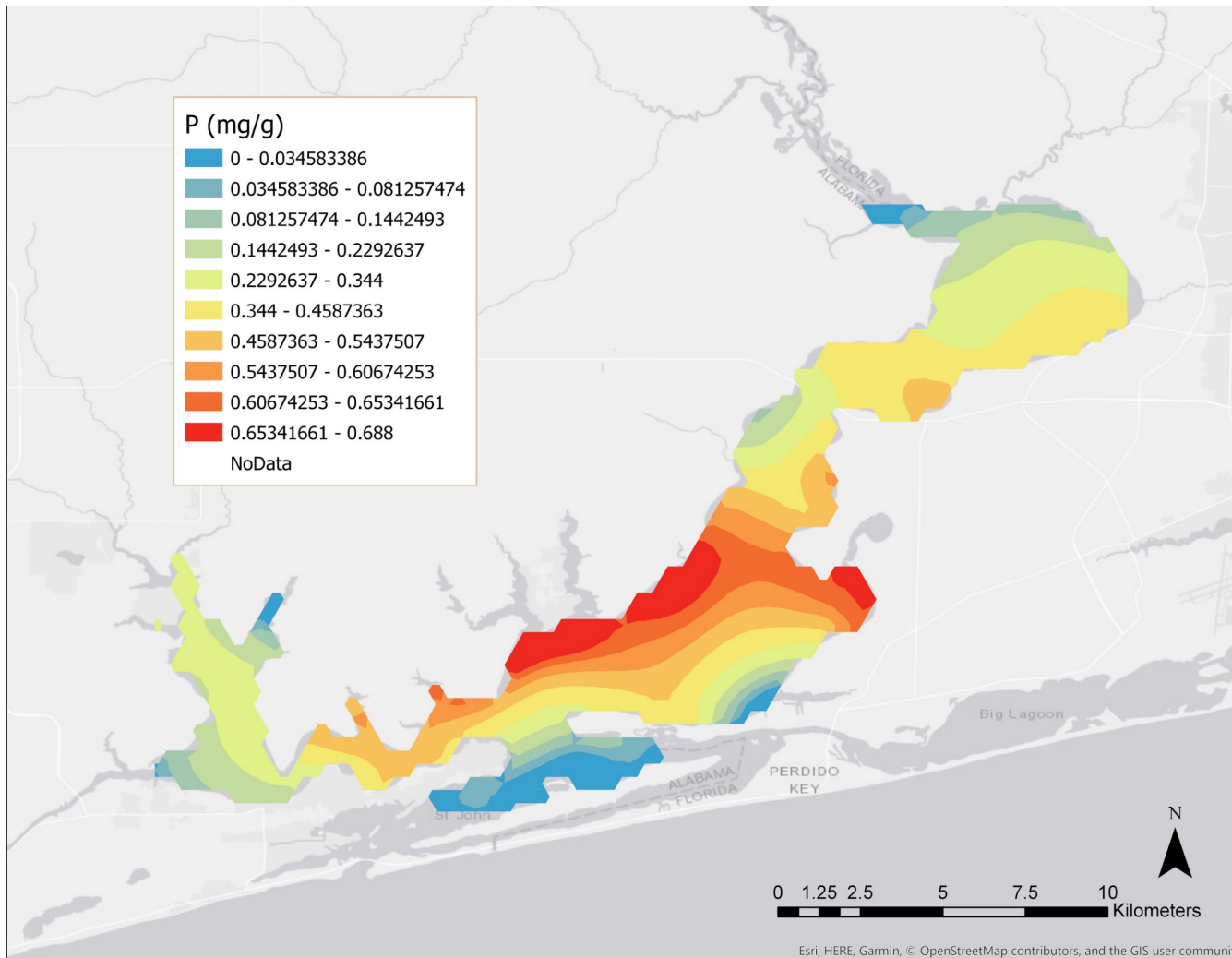


Figure 3.6. Interpolation of Sediment Total Phosphorus (P). Expressed in mg g^{-1} .

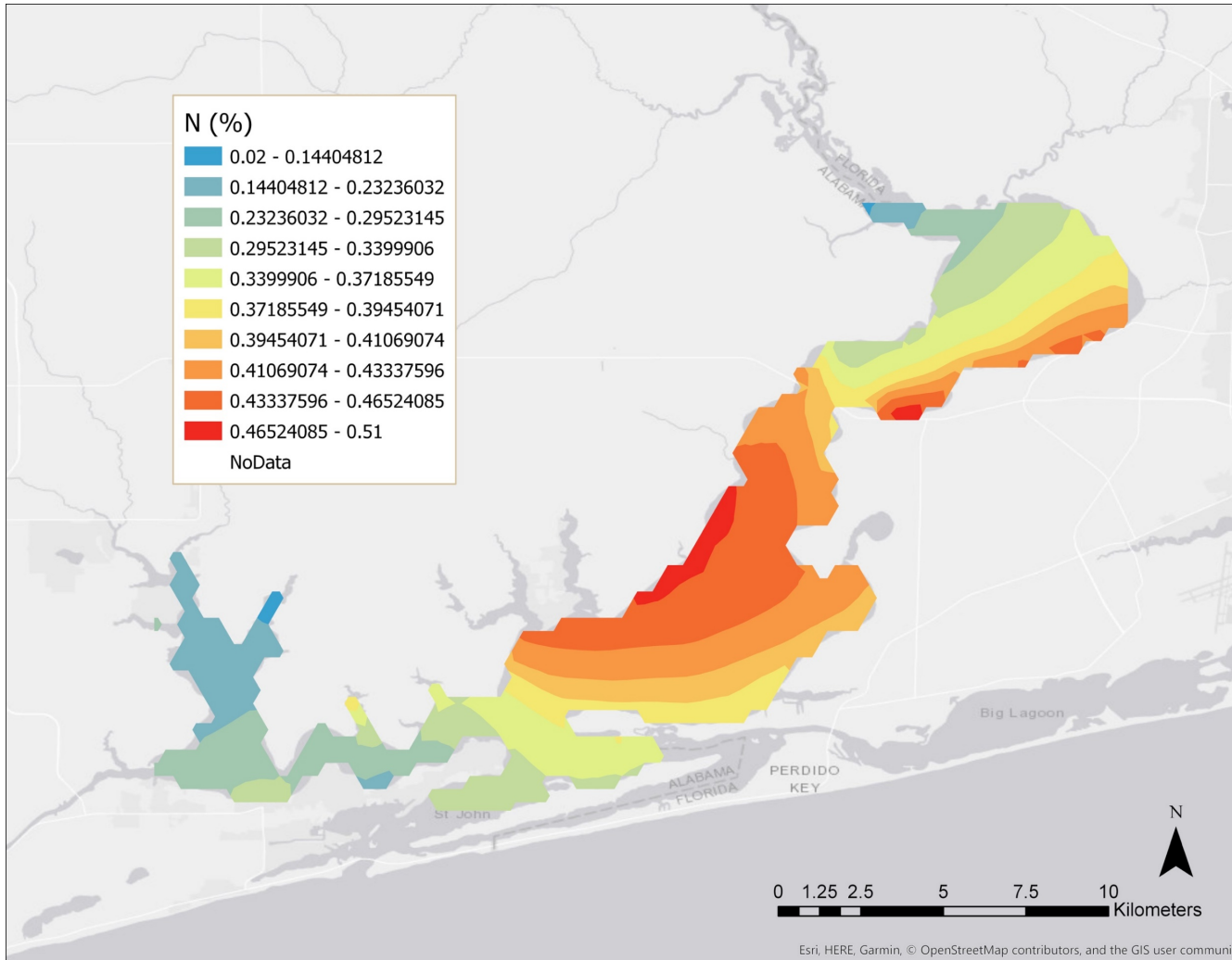


Figure 3.7. Interpolation of Sediment Total Nitrogen (N). Expressed as percentage (%).

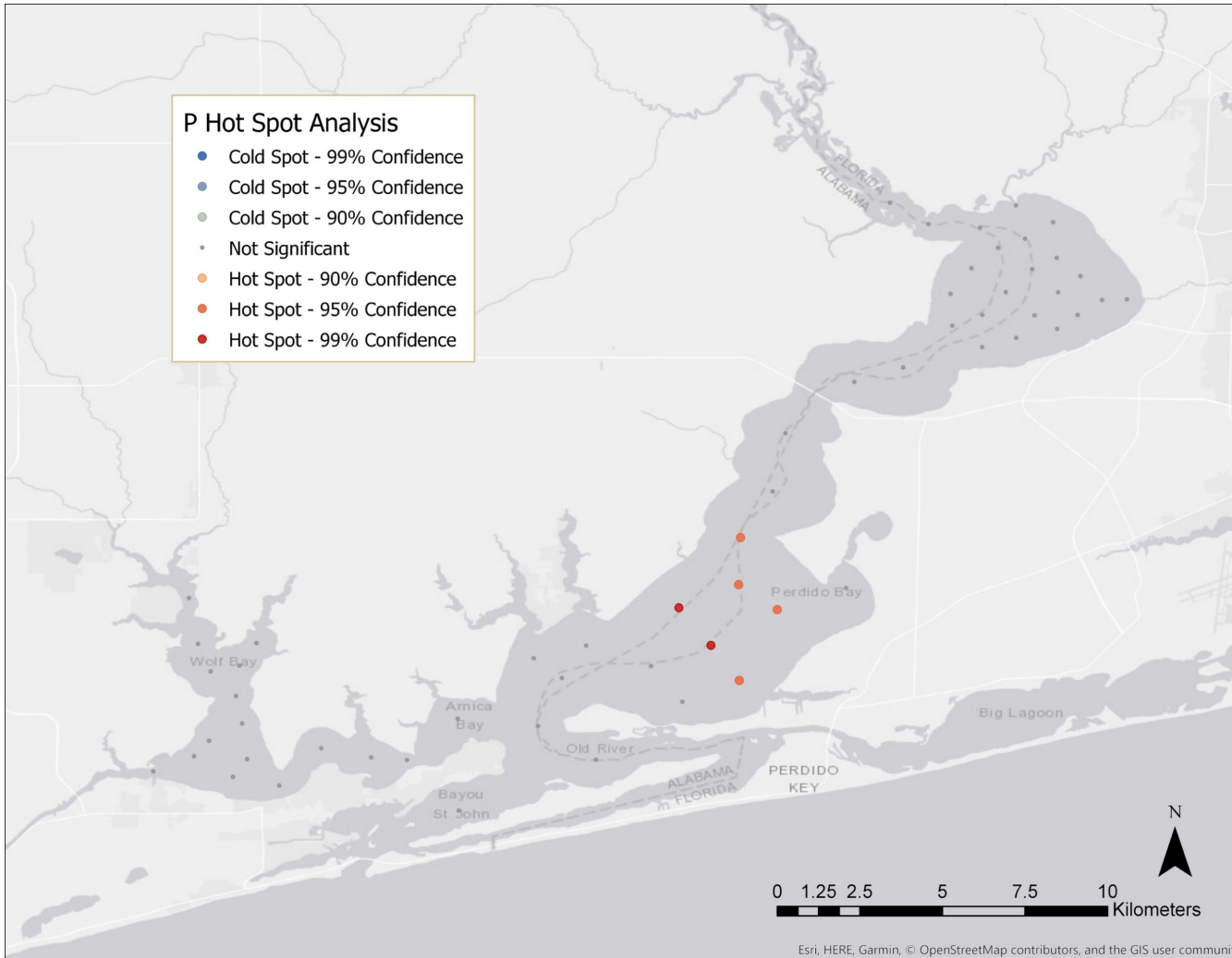


Figure 3.8. Phosphorus Hot Spot Analysis.

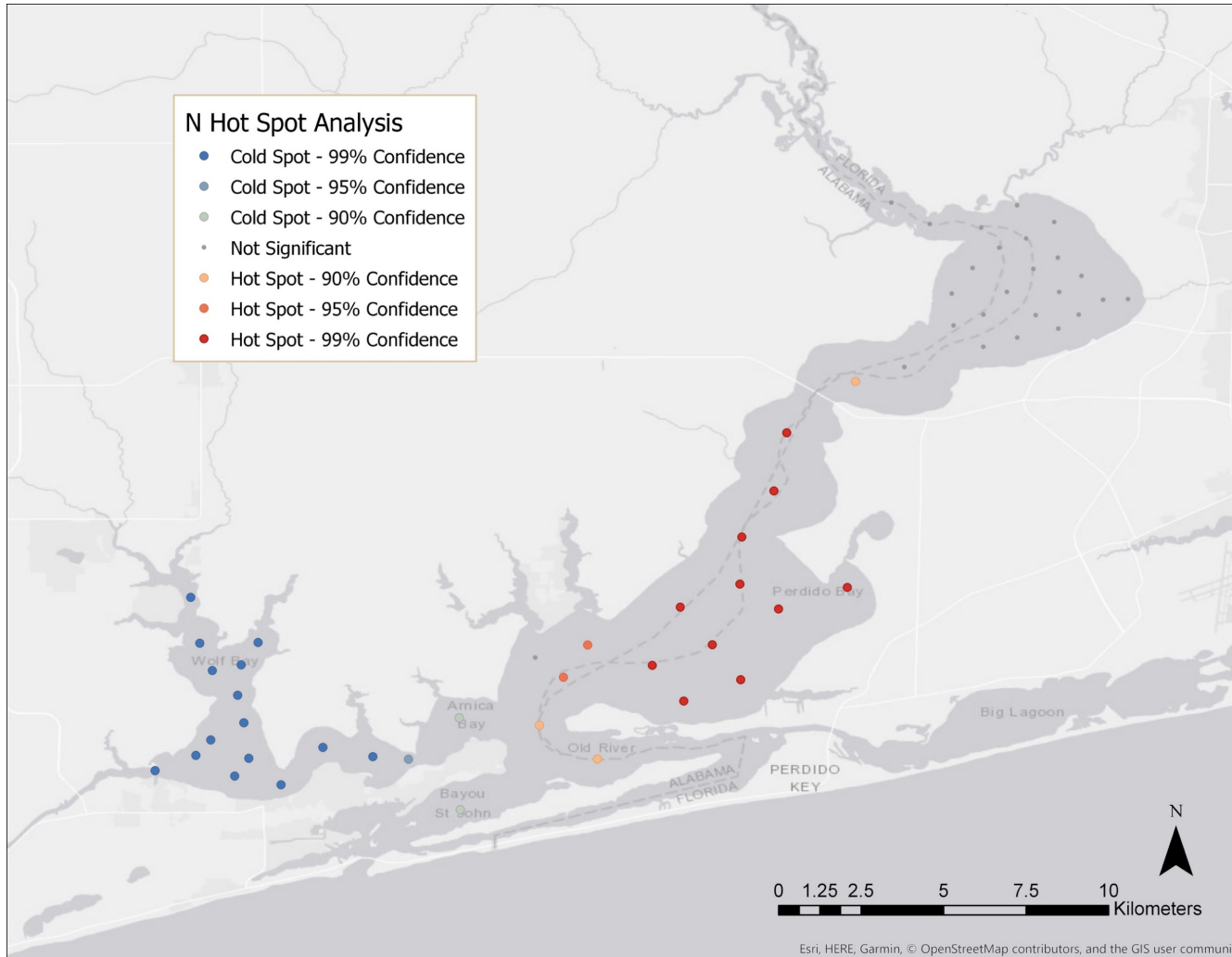


Figure 3.9. Nitrogen Hot Spot Analysis.

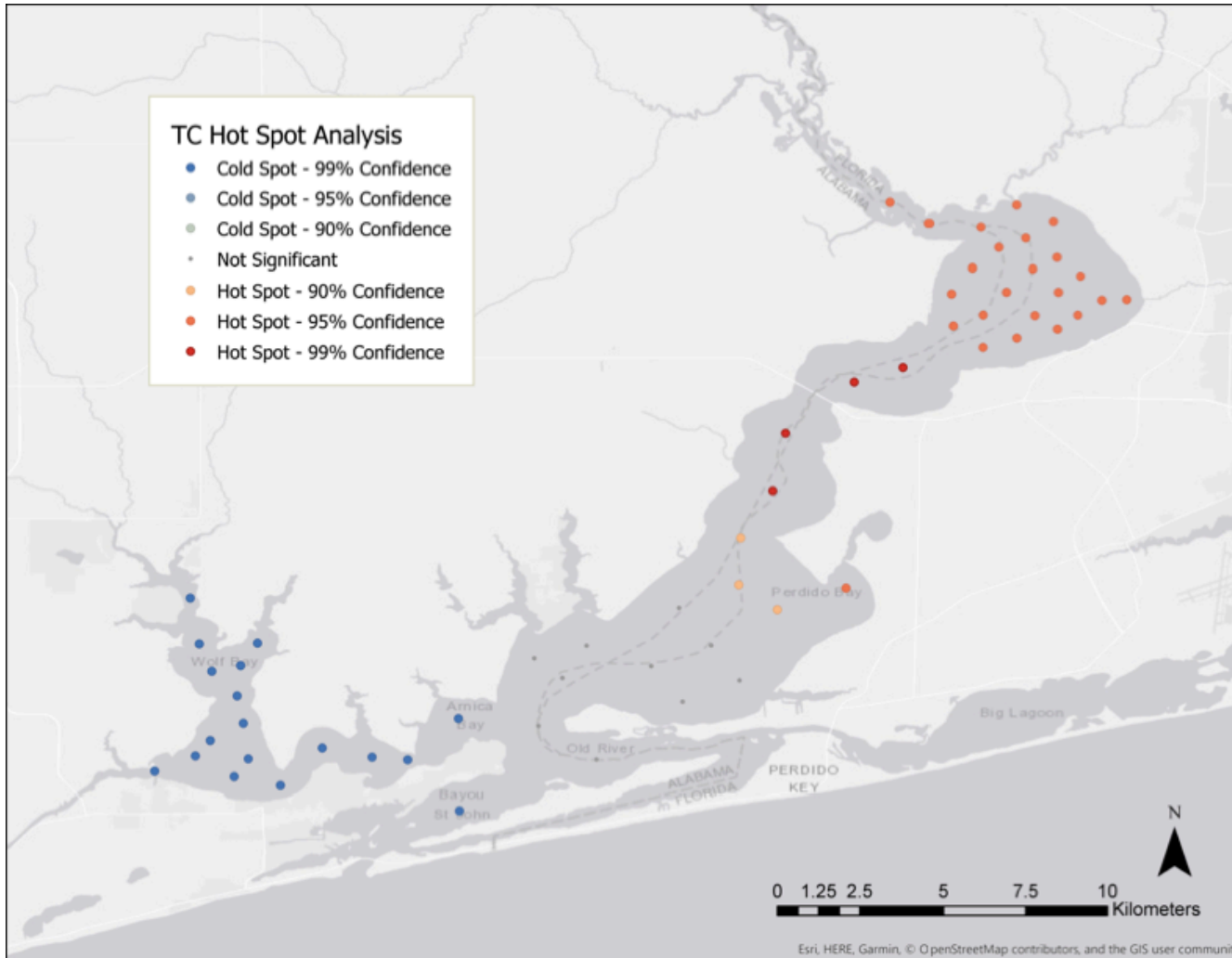


Figure 3.10. Carbon Hot Spot Analysis.

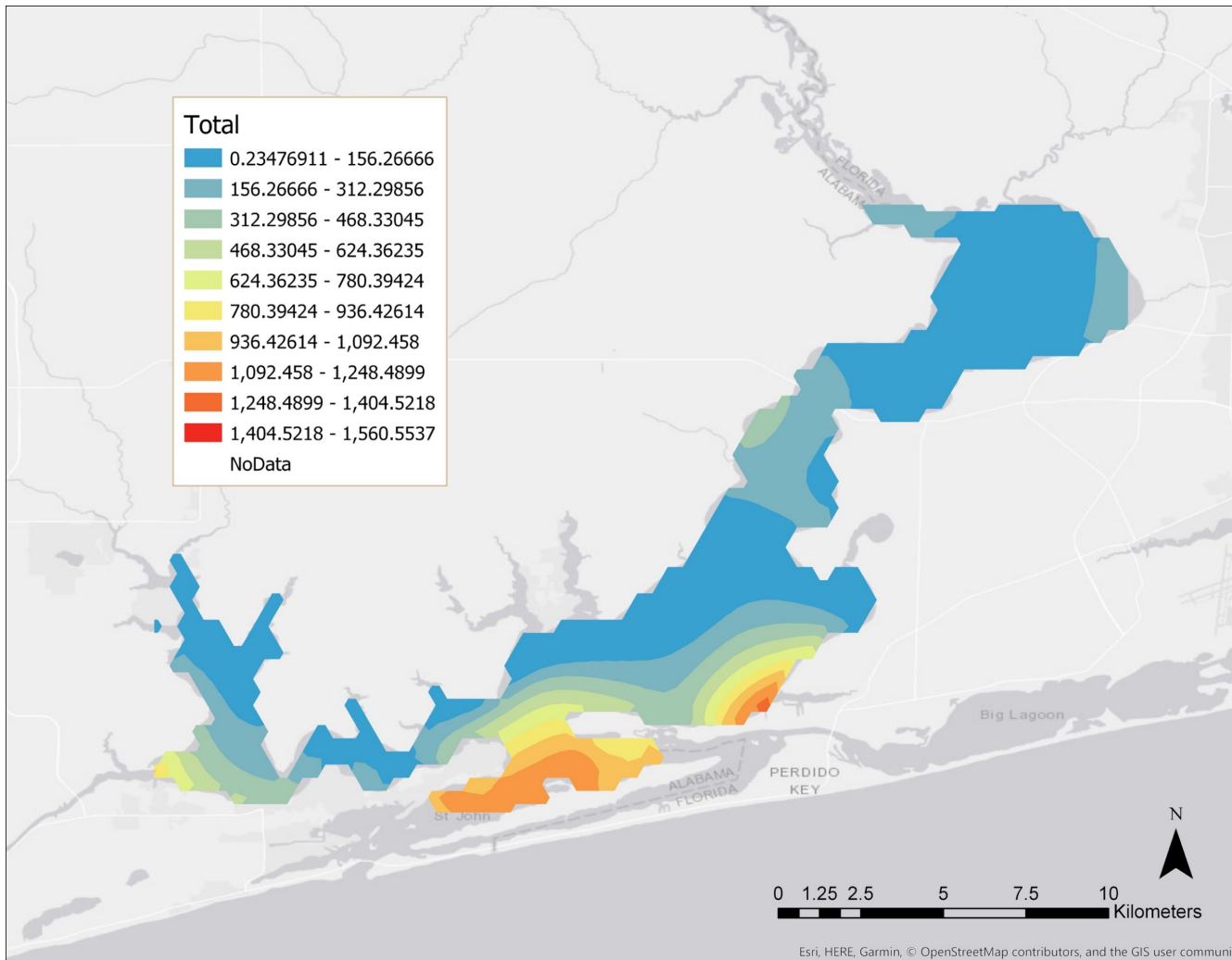


Figure 3.11. Interpolation of Total Chlorophylls (Total). Expressed as nmol g^{-1} organic matter.

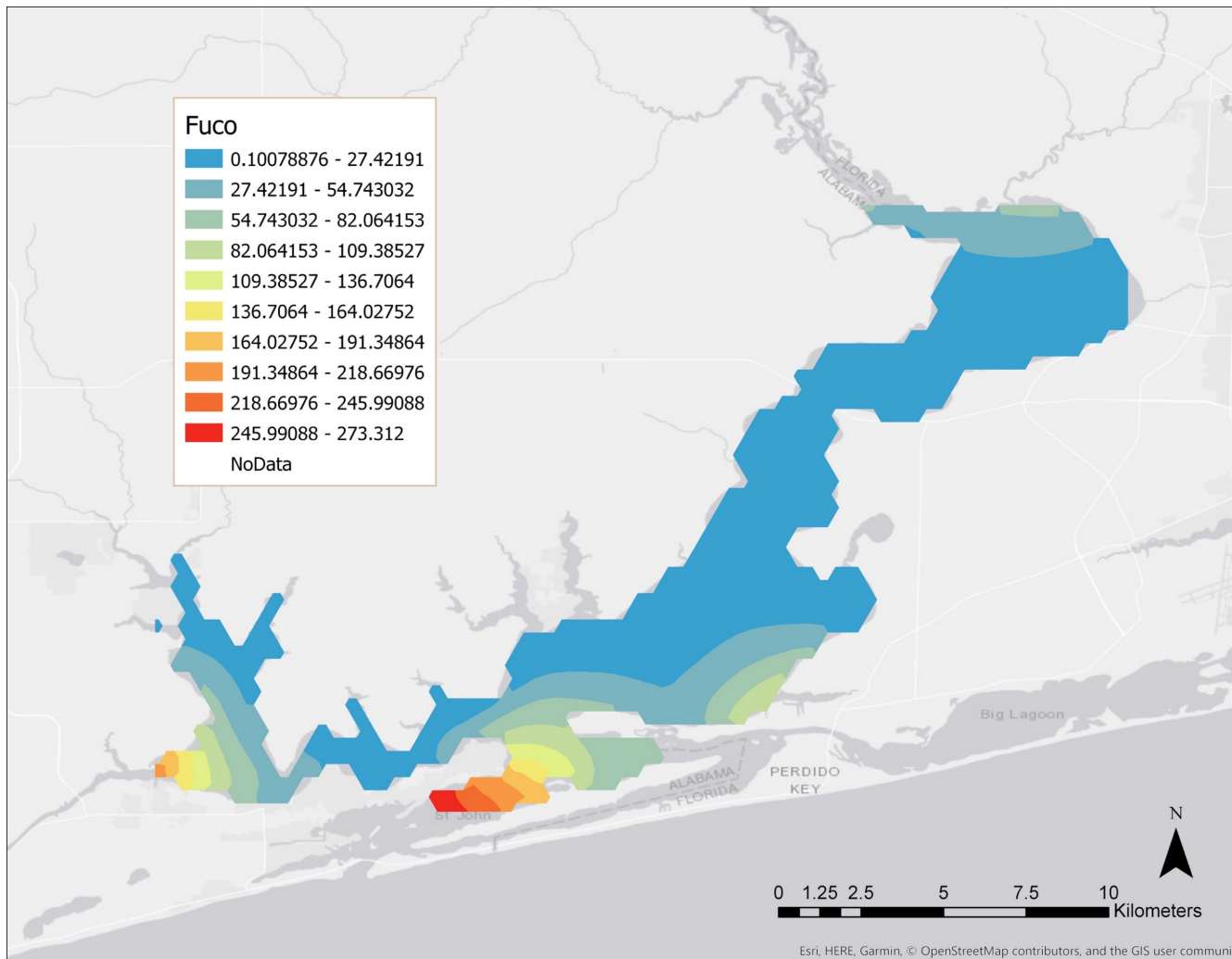


Figure 3.12. Interpolation of Fucoxanthin (Fuco). Expressed as nmol g^{-1} organic matter.

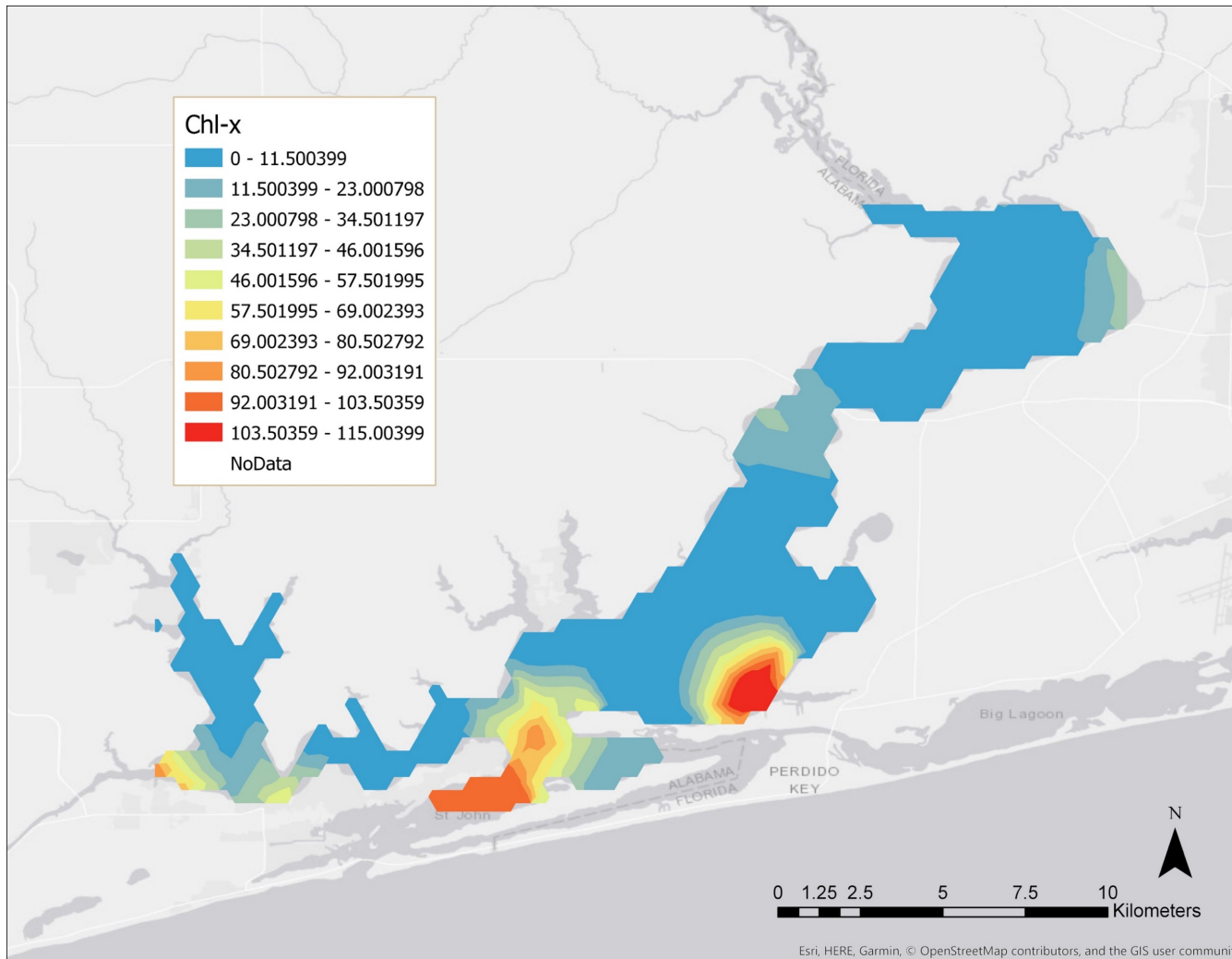


Figure 3.13. Interpolation of Chlorophyll-x (Chl-x). Expressed as nmol g^{-1} organic matter.

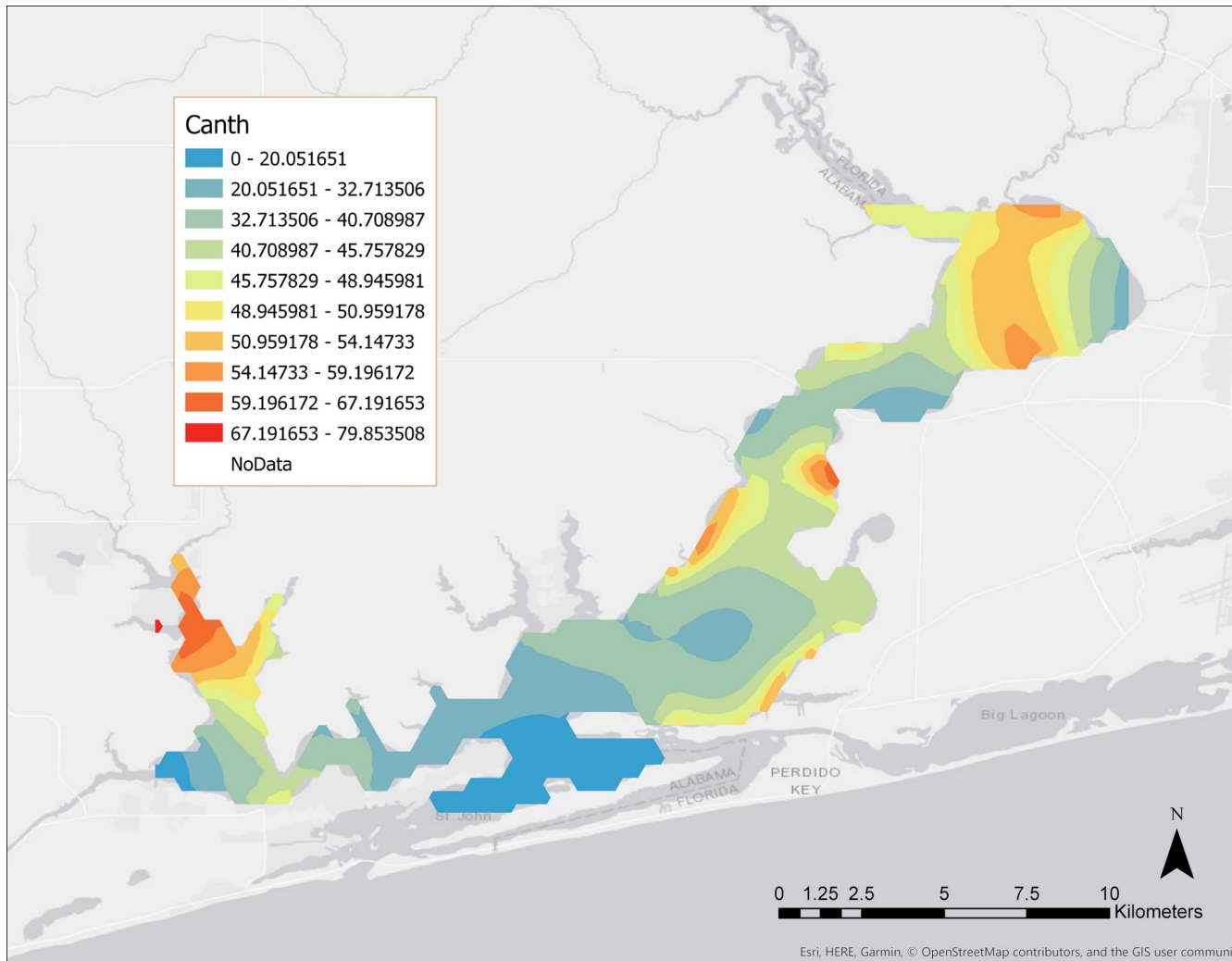


Figure 3.14. Interpolation of Canthaxanthin (Canth). Expressed as nmol g⁻¹ organic matter.

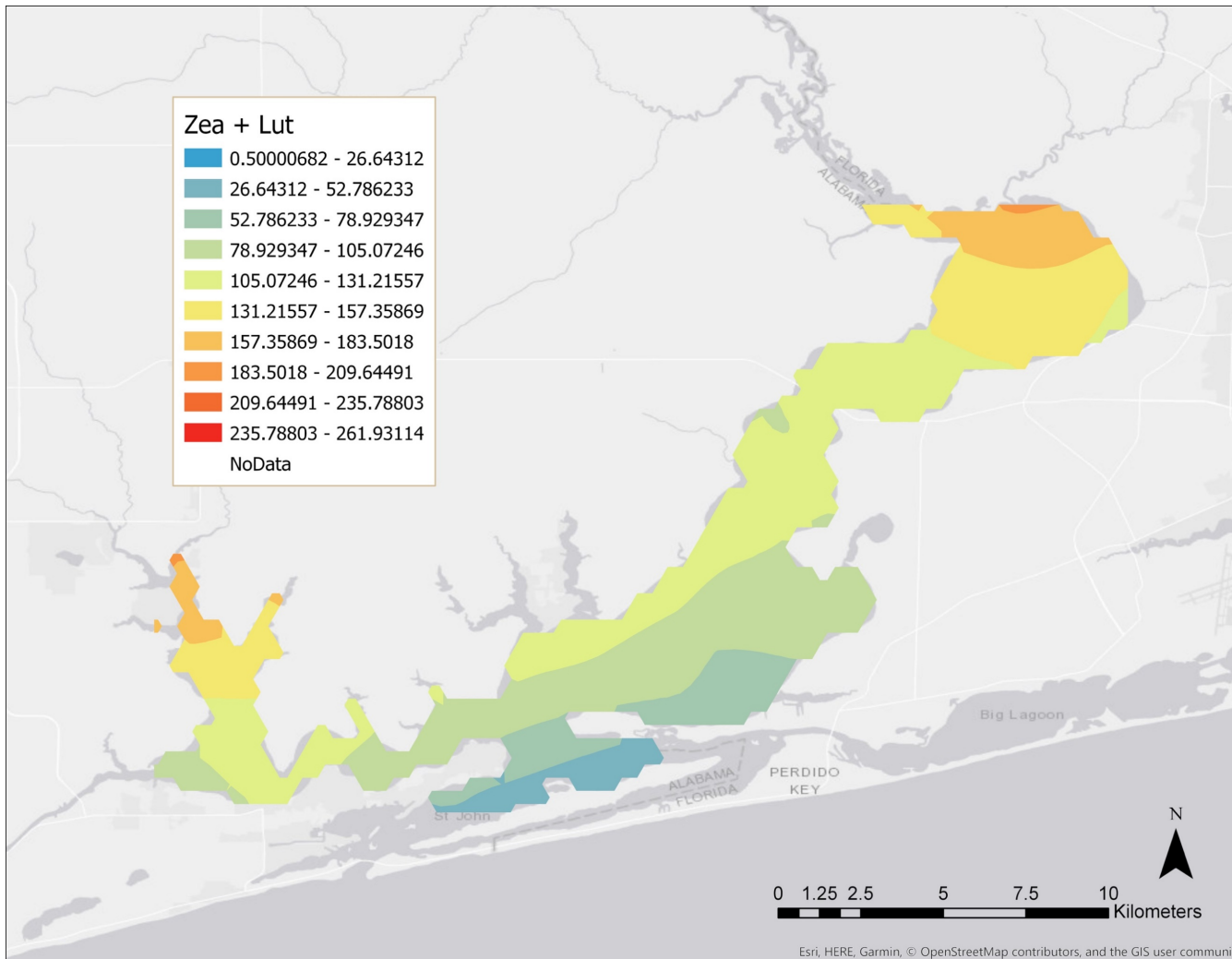


Figure 3.15. Interpolation of Zeaxanthin and Lutein (Zea+Lut). Expressed as nmol g^{-1} organic matter.

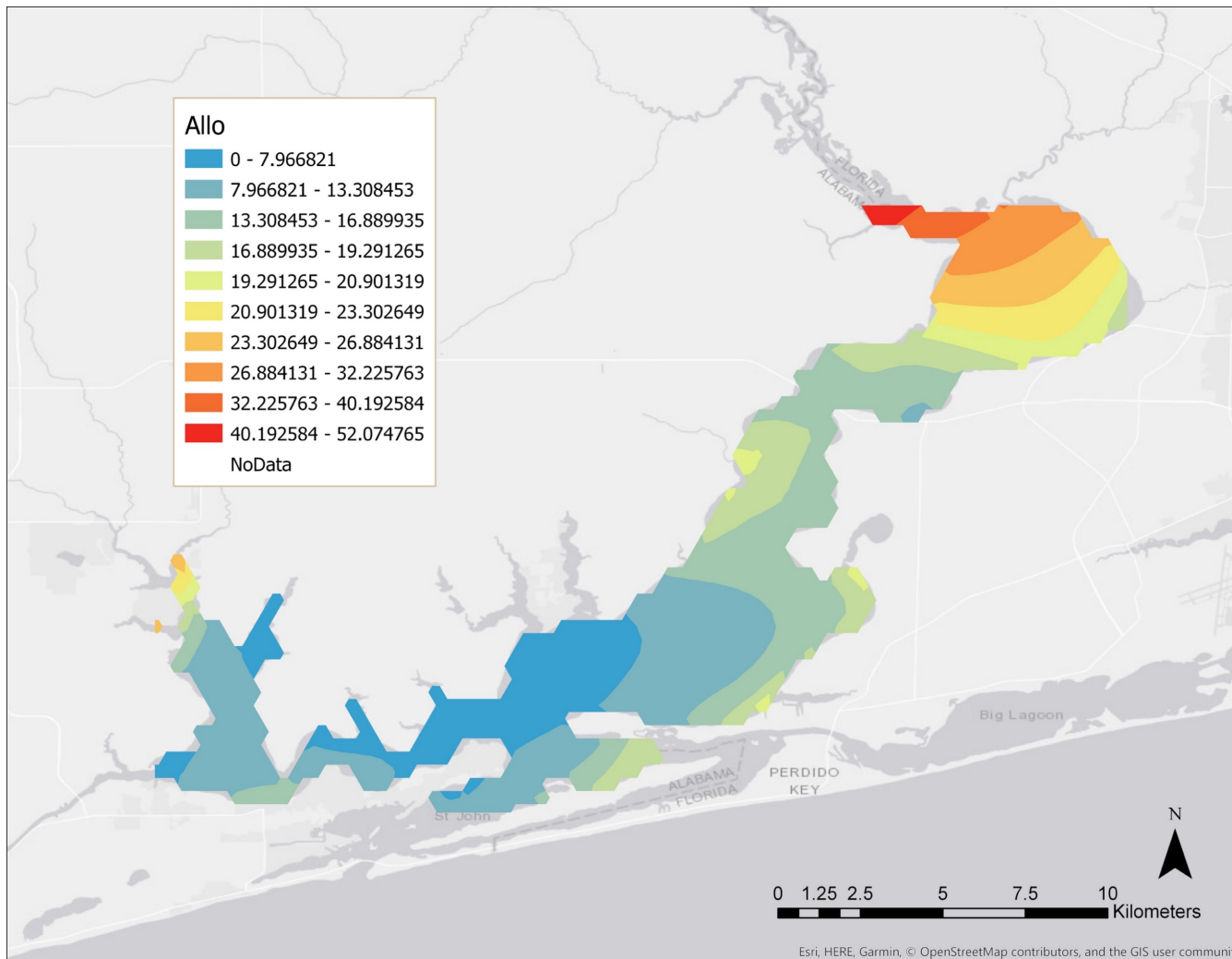


Figure 3.16. Interpolation of Alloxanthin (Allo). Expressed as nmol g^{-1} organic matter.

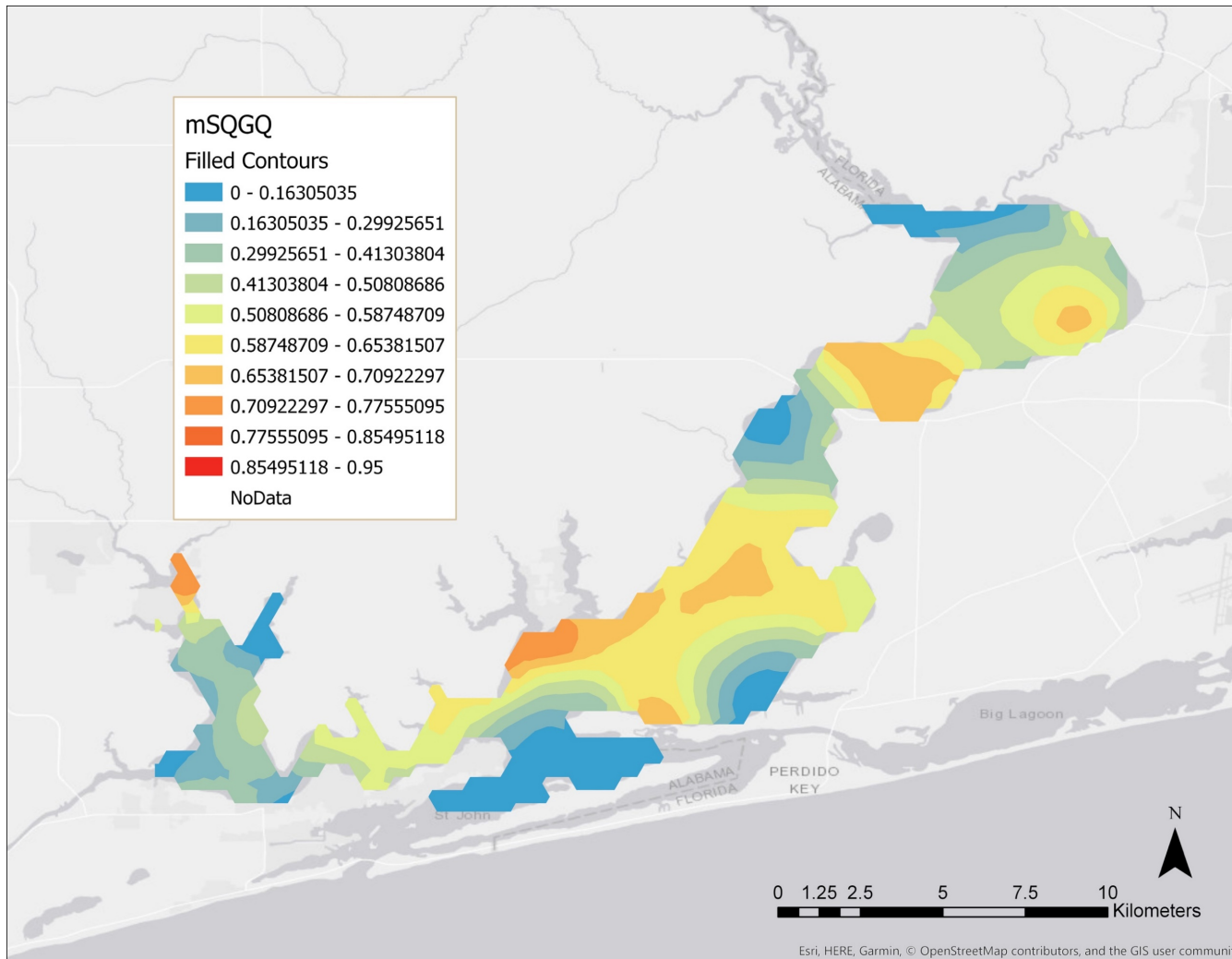


Figure 3.17. Interpolation of Mean Sediment Quality Guideline Quotient Values (mSQGs).

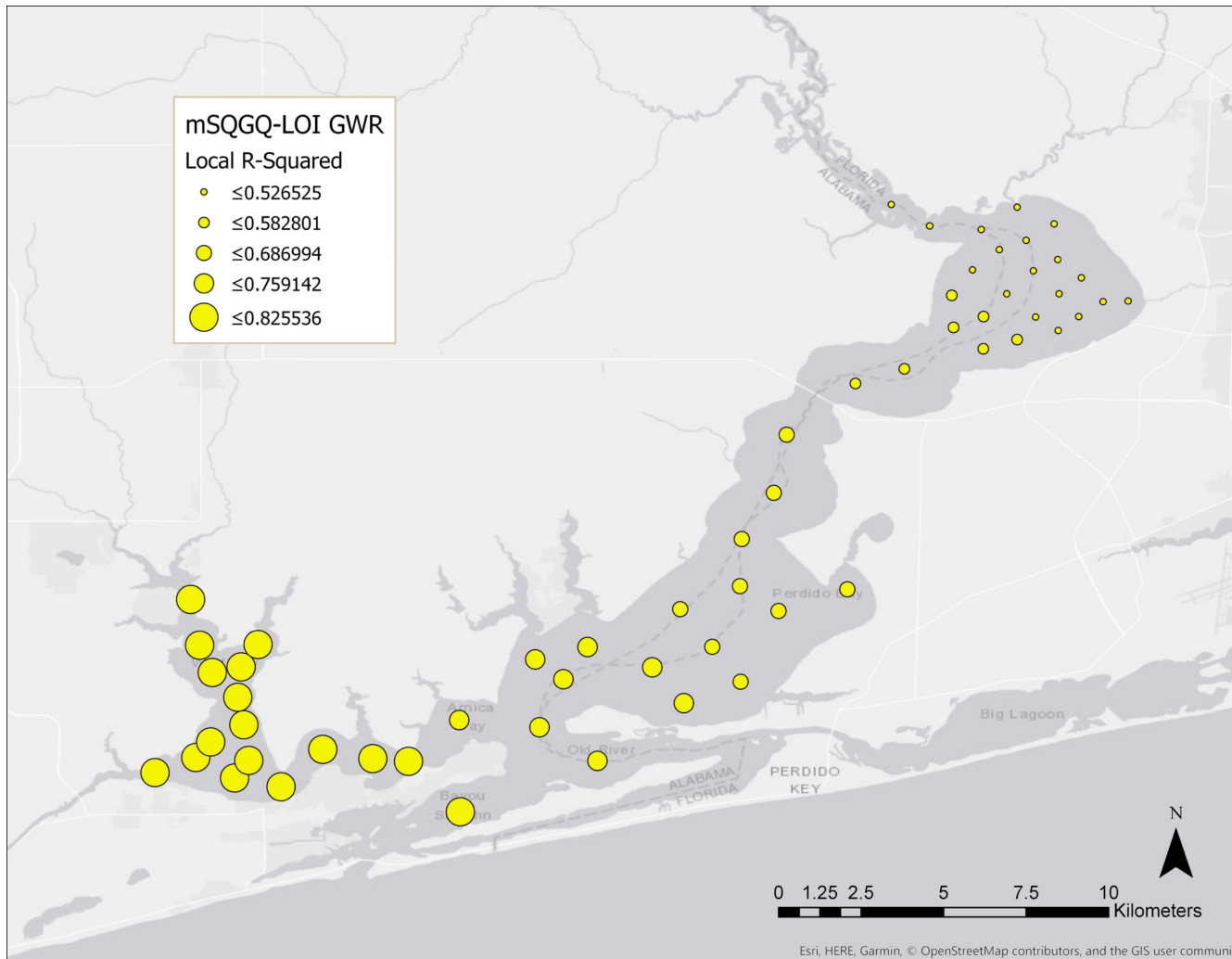


Figure 3.18. Local R^2 values between LOI and mSQGQ from Geographically Weighted Regression.

Chapter 4: Summary

Sediment cores and surface sediment samples from the Perdido and Wolf Bay areas yielded significant spatial and temporal differences throughout the system. While paleolimnological and sediment analyses are a relatively new source of data for coastal bay systems, my study showed that these techniques are viable tools to provide unique historical and spatial data not normally captured from monitoring programs. As a result, future applications could be used to determine stressors and drivers of change in other coastal bay systems and provide advice for future management strategies which require site-specific focus due to the distinctiveness of each estuary and the forces that act upon it.

Results from Chapter 2 (Fig. 2.5 & Fig. 2.7) indicate that significant increases in sediment and elemental deposition over time are discernable and can be predominantly attributed to the considerable changes in land use and land cover within the watershed histories of the two study sites. By combining the effects of agriculture and industry with the dramatic increase in population and development from 1960 until today, both bays reflect the multiplicity of anthropogenic stressors impacting most coastal systems. The beginning of increases in nutrient deposition appears to correspond more with the timing of the European colonization for Wolf Bay and Perdido Bay, but prominent increases throughout the sediment record further indicate that a combination of factors have had an additive effect over time. Phytoplankton abundance has also increased significantly over time in each bay as indicated by increases in photosynthetic pigment concentrations (Fig.

2.6 & Fig. 2.8). Wolf Bay experienced an extreme shift in primary producer abundance and community structure in the early 1930s, but Perdido Bay experienced a gradual increase in all measured pigments beginning before the dated history of the core (17th-18th century).

The primary driver of change in Wolf Bay was likely the dredging of the GIWW in the early 1930s which correlates with significant shifts in phytoplankton abundance (Fig. 2.6). Increased connectivity with Mobile Bay and phytoplankton within it could explain the observed changes, but the significant decrease in N:P (Fig. 2.5) indicates that loading of phosphorus also contributed to the eutrophication of Wolf Bay. The drivers of eutrophication in Perdido Bay are less well-defined since primary producer abundance has increased gradually throughout time (Fig. 2.8) indicating that a multiplicity of factors have influenced the decrease in ecosystem quality. Increasing inputs of nitrogen and phosphorus (Fig. 2.7) and a decreasing trend in C:N (Fig. 2.8) suggest that increased nutrient supply led to increased algal biomass being deposited in the sediments of Perdido Bay, but light limitation due to high DOC from riverine discharge likely heavily influences primary producer communities in the upper bay as supported by the findings of Chapter 3. Applying these data to future management of the system suggests that repercussions from any alterations of hydrology should be heavily researched beforehand and that recovery of the natural ecosystem state, while unlikely, will require significant reduction of nutrient loading to the estuaries.

Spatial analysis of sedimentary variables in Chapter 3 provided further insight on the spatial characteristics of pollutants and the distribution and drivers of phytoplankton communities throughout the greater Perdido Bay system. The study found nutrient and

heavy metal pollution to be more heavily linked with land use and organic matter deposition (Figs. 3.6, 3.7, 3.5) than phytoplankton abundance and that heavy metal conditions were found unlikely to be toxic to biota (Fig. 3.17). Furthermore, the importance of freshwater inflow on determining phytoplankton community structure was revealed. Cryptophytes and cyanobacteria were the dominant communities in DOC-rich waters of upper Perdido Bay (Fig. 3.16 & Fig 3.14) indicating that light attenuation is a limiting factor of eutrophication in the upper bay. Diatoms and brown algae were the dominant primary producers in the more seaward portions of the study area (Fig. 3.12), likely due to the presence of epiphytic and epipsammic communities living on seagrasses and within sand, respectively. Overall, measured phytoplankton abundance was considerably higher nearest marine inputs (Fig. 3.11), though those findings could have been biased by the collection of living algae rather than phytoplankton detritus in sediment samples collected in the clear-water conditions near the Gulf of Mexico.

The combination of temporal analysis in Chapter 2 and spatial analysis in Chapter 3 have provided a unique, multidisciplinary approach at understanding the complexity of the biogeochemical and ecological processes of a Gulf of Mexico estuary which has never been accomplished before. This study has provided novel findings at the local and regional scale including dredging of the GIWW as a driver of Wolf Bay eutrophication, organic carbon burial rates in an open water estuary rivalling those of coastal wetlands, and the use of geospatial tools to analyze more than just heavy metal concentrations in coastal sediments. Additionally, many of the conclusions of this study agreed with previous studies that utilized water sampling in various regions of the globe, demonstrating the effectiveness of sediment science in understanding the long-term

conditions of a coastal estuary without requiring sampling multiple times a day to encapsulate the effects of tidal action.

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