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Carbon and Nitrogen Stable Isotopic Patterns in South Florida Coastal Ecosystems: Modern and Paleooceanographic Perspectives

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

CARBON AND NITROGEN STABLE ISOTOPIC PATTERNS IN SOUTH FLORIDA
COASTAL ECOSYSTEMS: MODERN AND PALEOCEANOGRAPHIC
PERSPECTIVES

A dissertation submitted in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

in

GEOSCIENCES

by

Samantha L. Evans

2009

To: Dean Kenneth Furton
College of Arts and Sciences

This dissertation, written by Samantha L. Evans, and entitled Carbon and Nitrogen Stable Isotopic Patterns in South Florida Coastal Ecosystems: Modern and Paleoceanographic Perspectives, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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ABSTRACT OF THE DISSERTATION
CARBON AND NITROGEN STABLE ISOTOPIC PATTERNS IN SOUTH FLORIDA
COASTAL ECOSYSTEMS: MODERN AND PALEOCEANOGRAPHIC
PERSPECTIVES

by

Samantha L. Evans

Florida International University, 2009

Miami, Florida

Professor William T. Anderson, Major Professor

Long term management plans for restoration of natural flow conditions through the Everglades increase the importance of understanding potential nutrient impacts of increased freshwater delivery on coastal biogeochemistry. The present study sought to increase understanding of the coastal marine system of South Florida under modern conditions and through the anthropogenic changes in the last century, on scales ranging from individual nutrient cycle processes to seasonal patterns in organic material (OM) under varying hydrodynamic regime, to century scale analysis of sedimentary records. In all applications, carbon and nitrogen stable isotopic compositions of OM were examined as natural recorders of change and nutrient cycling in the coastal system.

High spatial and temporal variability in stable isotopic compositions were observed on all time scales. During a transient phytoplankton bloom, $\delta^{15}\text{N}$ values suggested nitrogen fixation as a nutrient source supporting enhanced productivity. Seasonally, particulate organic material (POM) from ten sites along the Florida Reef Tract and in Florida Bay demonstrated variable fluctuations dependent on hydrodynamic

setting. Three separate intra-annual patterns were observed, yet statistical differences were observed between groupings of Florida Bay and Atlantic Ocean sites. The POM $\delta^{15}\text{N}$ values ranged on a quarterly basis by 7‰, while $\delta^{13}\text{C}$ varied by 22‰. From a sediment history perspective, four cores collected from Florida Bay further demonstrated the spatial and temporal variability of the system in isotopic composition of bulk OM over time. Source inputs of OM varied with location, with terrestrial inputs dominating proximal to Everglades freshwater discharge, seagrasses dominating in open estuary cores, and a marine mixture of phytoplankton and seagrass in a core from the boundary zone between Florida Bay and the Gulf of Mexico. Significant shifts in OM geochemistry were observed coincident with anthropogenic events of the 20th century, including railroad and road construction in the Florida Keys and Everglades, and also the extensive drainage changes in Everglades hydrology. The sediment record also preserved evidence of the major hurricanes of the last century, with excursions in geochemical composition coincident with Category 4-5 storms.

TABLE OF CONTENTS

CHAPTER	PAGE
1 INTRODUCTION	1
1.1 BACKGROUND	2
1.1.1 Florida Bay	2
1.1.2 Florida Keys Reef Tract, Florida Keys National Marine Sanctuary	8
1.1.3 Stable Isotopes of Carbon and Nitrogen	10
1.2 RATIONALE	15
1.3 HYPOTHESES	17
1.4 OBJECTIVES	18
1.5 DISSERTATION ORGANIZATION	19
LITERATURE CITED	20
2 SPATIAL VARIABILITY IN FLORIDA BAY PARTICULATE ORGANIC MATTER COMPOSITION: COMBINING FLOW CYTOMETRY WITH STABLE ISOTOPE ANALYSES	27
2.1 ABSTRACT	28
2.2 INTRODUCTION	29
2.3 METHODS	33
2.3.1 Setting	33
2.3.2 Sampling Locations and Collection	34
2.3.3 Flow Cytometry Analyses	35
2.3.4 Isotopic Analyses	36
2.3.5 Nutrient Analyses	37
2.4 RESULTS	37
2.5 DISCUSSION	42
2.6 CONCLUSION	50
LITERATURE CITED	53
3 SPATIAL AND TEMPORAL VARIABILITY IN THE ISOTOPIC COMPOSITION OF PARTICULATE ORGANIC MATERIAL: SOURCES, CONTROLS, AND EPISODIC CHANGE	58
3.1 ABSTRACT	59
3.2 INTRODUCTION	60
3.3 METHODS	65
3.3.1 Sampling Protocol	65
3.3.2 Flow Cytometer Analyses	67
3.3.3 Statistical Analyses	68
3.4 RESULTS	68
3.4.1 Time Series	68
3.4.2 Size Class Variability	78
3.4.3 Source indicators of POM	85
3.5 DISCUSSION	87

3.5.1	Temporal variability and hydrodynamic regime	91
3.5.2	POM isotopic variability and water quality parameters	96
3.5.3	Florida Bay versus Atlantic Ocean pooled site characteristics	98
3.5.4	Size fractionated sampling isotopic implications	103
3.6	CONCLUSIONS	106
	LITERATURE CITED	108
4	STABLE ISOTOPE COMPOSITION OF SEDIMENTARY ORGANIC MATTER FROM FLORIDA BAY	117
4.1	ABSTRACT	118
4.2	INTRODUCTION	119
4.3	METHODS	123
4.3.1	Setting	123
4.3.2	Sample Collection	123
4.3.3	Geochemical Analyses	124
4.3.4	Age Dating of Sediment Cores	126
4.3.5	Statistical Analyses	127
4.4	RESULTS	128
4.4.1	Trout Creek Sediment Geochemistry	129
4.4.2	Russell Bank Sediment Geochemistry	130
4.4.3	Bob Allen Bank Sediment Geochemistry	131
4.4.4	Ninemile Bank Sediment Geochemistry	133
4.4.5	Organic carbon, total nitrogen, and total phosphorus content	134
4.4.6	Carbon and nitrogen isotopic signatures	137
4.5	DISCUSSION	139
4.5.1	Isotopic and elemental source characterization	139
4.5.2	Anthropogenic influences on Florida Bay over time	147
4.5.3	Hurricane history	151
4.6	CONCLUSIONS	157
	LITERATURE CITED	159
5	CONCLUSIONS AND FUTURE STUDIES	168
5.1	CONCLUSION	169
5.2	ISOTOPIC VARIABILITY IN POM	170
5.2.1	Nitrogen fixation in transient cyanobacterial blooms	170
5.2.2	Spatial and temporal isotopic variability in size-fractionated POM	171
5.2.3	Limitations of the POM time-series	173
5.3	FLORIDA BAY SEDIMENTARY RECORDS	175
5.4	FUTURE STUDIES	177
	LITERATURE CITED	179
	APPENDICES	181
	VITA	209

LIST OF TABLES

TABLE		PAGE
Chapter 2	Table 2.1 Mean and S.D. of phytoplankton and bacteria population abundances determined by logical gating (Win MDI; Trotter 1994-2000) for samples collected during the Nov. 2003 Florida Bay snapshot POM sampling. All values are cells ml ⁻¹ * 10 ³	39
Chapter 3	Table 3.1 POM sampling site locations and mean depths	66
	Table 3.2 Descriptive statistics for each POM size fraction collected from 10 sites in Florida Bay and the Florida Keys National Marine Sanctuary	70
	Table 3.3 Differences between size fractions: ANOVA P-Values	78
Chapter 4	Table 4.1 Florida Bay core locations, calculated average sedimentation rate, core length recovered, and depth with age constraints by ²¹⁰ Pb chronology	125
	Table 4.2 δ ¹³ C (‰), δ ¹⁵ N (‰) (Mean ± SD)	128
	Table 4.3 Percent elemental compositions and calculated molar ratios for each core (Mean ± SD)	137
	Table 4.4 Sediment geochemical parameter means ± st. dev. comparing pre- and post-1910 data sets	138
	Table 4.5 Representative isotopic and elemental compositions of terrestrial verses marine organic matter sources to Florida Bay	141

LIST OF FIGURES

FIGURE	PAGE
Chapter 2	
Figure 2.1	Map of Florida Bay, showing sampling locations in Western Florida Bay at Sprigger Bank (1) and Ninemile Bank (2), in Northeastern Florida Bay at South Nest Key (3) and Duck Key (4), and near the Taylor Slough Everglades outflow at Trout Creek (5). 33
Figure 2.2	Flow cytometry analyses of Florida Bay phytoplankton collected at five sampling locations in Western (a-d) and Northeastern (e-h) Florida Bay, and proximal to the Everglades outflow (i-j). 38
Figure 2.3	Flow cytometry analyses of November, 2003, Florida Bay surface water bacteria samples after DNA staining with SYBR Green. 41
Figure 2.4	Stable isotope signals in 0.1-50 μ m POM collected in November 2003. 43
Chapter 3	
Figure 3.1	Map of Florida Bay and the Florida Keys National Marine Sanctuary, showing POM sampling sites on the Atlantic Ocean side of the Florida Keys: Carysfort Reef (215), Molasses Reef (225), Tennessee Reef (243), Coffins Patch Channel (248), Bahia Honda Channel (255); and in Florida Bay: Tripod Bank (284), Bamboo Bank (287), Sprigger Bank (SP), Bob Allen Bank (BA), and Duck Key (DK). 66
Figure 3.2	Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from reef settings in the northern Florida Keys. 69
Figure 3.3	Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from reef and channel settings in the Middle Florida Keys. 72
Figure 3.4	Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from a channel setting in the Middle Florida Keys. 73

Figure 3.5	Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from shallow mudbank settings in Western Florida Bay.	74
Figure 3.6	Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from a shallow mudbank setting in Western Florida Bay.	75
Figure 3.7	Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from shallow mudbank settings proximal to both islands and Everglades outflows in Northeastern and Central Florida Bay.	76
Figure 3.8	Mean annual patterns in $\delta^{15}\text{N}$ values; 2 years combined.	77
Figure 3.9	Variation in $\delta^{13}\text{C}$ between POM size fractions combining ten sampling intervals.	80
Figure 3.10	Variation in $\delta^{15}\text{N}$ between POM size fractions combining ten sampling intervals.	81
Figure 3.11	Variation in $\delta^{15}\text{N}$ between POM size fractions during individual sampling intervals.	82
Figure 3.12	Bivariate isotope plots of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ for the three size fractions.	84
Figure 3.13	Bivariate plots of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ with Molar C:N ratio for the three size fractions.	86
Figure 3.14	Flow cytometry analyses of Florida Keys Reef Tract phytoplankton collected quarterly at 5 stations along a N-S transect down the Florida Keys.	88
Figure 3.15	Flow cytometry analyses of Florida Bay phytoplankton collected quarterly at 5 stations in the bay.	89
Figure 3.16	Conceptual model illustrating the distribution of South Florida coastal hydrodynamic zones as they influence nutrient dynamics and POM isotopic composition over time.	93

	Figure 3.17	Bivariate plots of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ with Log Chlorophyll- <i>a</i> for the 50-150 μm size fraction, dominated by autotrophic diatoms and dinoflagellates.	102
	Figure 3.18	Isotopic values of size fractionated and bulk POM samples collected at Molasses Reef (this study) and Dixie Shoals (purple circles, Lamb 2006; collected in 2000-2002).	104
Chapter 4	Figure 4.1	Map of Florida Bay, showing core collection sites at Ninemile Bank, Bob Allen Key, Russell Bank, and Trout Creek.	125
	Figure 4.2	Geochemical dataset from the upper 92 cm of a core collected from the mouth of Trout Creek, Northeastern Florida Bay.	129
	Figure 4.3	Geochemical dataset from a 166 cm long core collected at Russell Bank, Central Florida Bay.	130
	Figure 4.4	Geochemical dataset from the upper 66 cm of a core collected from Bob Allen Bank, Central Florida Bay.	132
	Figure 4.5	Geochemical dataset from the upper 66 cm of a core collected from Ninemile Bank, Western Florida Bay.	133
	Figure 4.6	Sediment elemental composition data over time at four sites in Florida Bay expressed in weight %.	136
	Figure 4.7	Carbon and nitrogen isotopic data from four Florida Bay cores: Bob Allen Bank (BA), Russell Bank (RB), Trout Creek (TC), and Ninemile Bank (9M).	138
	Figure 4.8	Carbon isotopic data from all Florida Bay cores plotted with two ^{13}C datasets from Swart et al., a coral record (Swart et al. 1996) and a sclerosponge record (Swart et al. 2002).	149
	Figure 4.9	Carbon and nitrogen isotope stratigraphy from the four Florida Bay cores highlighting isotopic evidence of hurricane disturbance.	153

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

South Florida's coastal environment represents a diverse and interconnected range of geomorphological settings and biological habitat types; transitioning from the fresh to brackish water mangrove ecotone through the shallow estuarine environment of Florida Bay to channel settings between the Florida Keys islands and beyond to the coral reef and hardbottom systems of the Atlantic nearshore zone. Over the past 50 to 100 years, all of these environments have been impacted by enormous changes in urbanization and population growth in South Florida, which have led to significant changes in the hydrology of the system and anthropogenic nutrient delivery. The present study has sought to increase understanding of these interconnected systems both under modern conditions and through the course of anthropogenic change in the last century, on scales ranging from individual processes of nutrient cycling to seasonal patterns in particulate organic material under varying hydrodynamic regime, to century-scale analysis of sedimentary records. In all these applications, carbon and nitrogen stable isotopic compositions of organic material have been examined as natural recorders of change and nutrient cycling in the coastal zone.

1.1.1 Florida Bay

Florida Bay is a shallow estuarine lagoon of $>2200 \text{ km}^2$ in areal extent lying between the South Florida mainland and the Florida Keys. The bay is bounded to the north with the mangrove wetlands of the southern Everglades, to the west with the open marine systems of the Southwest Florida Shelf and Gulf of Mexico, and to the south by the islands of the Florida Keys, connected via several channels to the coastal Atlantic and

the Florida Reef Tract. Thus, Florida Bay represents a dynamic region of exchange for three distinct hydrologic systems in South Florida.

The bay itself consists of a series of shallow basins (<3 m depth) separated hydrologically by a network of subtidal mudbanks and mangrove islands which restrict water mixing between basins and attenuate both tidal amplitude and current. Freshwater runoff, comparatively rich in dissolved inorganic nitrogen (DIN) and poor in soluble reactive phosphorus (SRP), enters this hydrologically complex system primarily in Northeastern Florida Bay through the Taylor Slough and the C-111 basin. Saline ocean water, comparatively depleted in DIN and enriched in SRP, enters across the western boundary with the Gulf of Mexico and through numerous tidal channels crossing the Florida Keys (Boyer et al. 1999). Interaction between these inflows and limitations on the bay's mixing regime serve to generate gradients in both salinity and nutrient availability across the bay.

Florida Bay has been influenced by changes in the timing and volume of freshwater flow from the Everglades in the last half century as a result of extensive modification of the natural discharge patterns by water management canalization and levee construction (Davis and Ogden 1994, Rudnick et al. 1999). These hydrological changes have prompted researchers to explore the extent to which salinity levels in the bay have been affected by these changes (Huvane 2002). Further, human alteration of the Everglades watershed in favor of agriculture and urbanization may have increased nutrient loads to downstream Florida Bay, adding research questions investigating impacts of this cultural eutrophication in the system (Fourqurean et al. 1993, Boyer et al. 1999). Historically, the Florida Bay ecosystem is thought to have been a shallow,

optically clear lagoon characterized by low nutrient levels and populated by abundant seagrass communities. However, in recent years significant changes have been observed in water clarity, hypersaline conditions have periodically developed during summer months, and widespread die offs have occurred in the seagrass communities, coincident with extensive phytoplankton blooms (Robblee et al. 1991, Philips and Badylak 1996, Philips et al. 1999, Glibert et al. 2004). Although there has been growing concern that biotic shifts are related to anthropogenic changes in Everglades flow and increasing nutrient inputs from the Florida Keys and the Gulf of Mexico, it is also questioned whether the changes are a consequence of natural phenomena, such as climatic fluctuation or ecological succession cycles (Lapointe and Clark 1992, McIvor et al. 1994, Lapointe et al. 1994, Swart et al. 1999).

Long term proxy records of environmental change, for example those found in coral skeletons (Smith et al. 1989, Swart et al. 1996, Swart et al. 1999) and those in sedimentary records (Halley and Roulier 1999, Brewster-Wingard and Ishman 1999, Brewster-Wingard et al. 2001, Huvane and Cooper 2001, Cronin et al 2001, Xu et al. 2007), can provide a baseline understanding of how the South Florida system has changed through time over the last 100 to 3000 years, however there is some discordance between different proxies. Coral fluorescence and isotopic values ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) recorded in annular growth rings from *Solenastrea bournoni* corals from Lignumvitae Basin both imply that there has been no long term change in salinity over the last 175 years, however changes in water management practices circa 1940 were in fact recorded in fluorescence patterns (Smith et al. 1989, Swart et al. 1999). A slight increase in salinity coincident with restriction in circulation related to closure of Florida Keys

channels during construction of the Overseas Railway (1907-1912) was also evident in coral isotopic records (Swart et al. 1999). In contrast to the salinity reconstruction of Swart et al. (1996), Brewster-Wingard and Ishman (1999) and Brewster-Wingard et al. (2001) demonstrated that the average salinity of Florida Bay has been increasing since 1880 and that salinity fluctuations have been more frequent and of greater amplitude since the beginning of the 20th century based on molluscan and foraminiferal assemblages in several cores from central Florida Bay. Additionally, the presence of the euryhaline bivalve, *Brachiodontes*, also tolerant of decreases in water quality (i.e. increasing nutrient content and decreasing water clarity) indicates deterioration of the ecosystem after water management structures were implemented in the Everglades watershed beginning in 1930. Similar findings were reported by Huvane and Cooper (2001) based on diatom assemblage changes in central and NE Florida Bay cores. The reliable chronology of these studies extended less than 200 years, but changes in speciation around 1940 imply increases in salinity related to canalization of the Everglades and ensuing reduction of freshwater discharge to Florida Bay. Increases in the ratio of planktonic to benthic diatoms observed since 1940 also suggest declining water quality, as planktonic algal blooms are related to increases in nutrient availability. Decreases in epiphytic diatom populations suggest declines in seagrass habitat over time, consistent also with correlations to declining water quality in Florida Bay in the past 100 years.

In light of the eight billion dollar Comprehensive Everglades Restoration Project (CERP) and current efforts to restore the Everglades ecosystem, including Florida Bay, to a “pristine” state, it is important to understand the natural state of the system. Quantitative meteorological, ecological, and water quality datasets extend only to the

1950s, post-dating many significant anthropogenic alterations of the system, thus paleoecological and paleoceanographic reconstructions have become increasingly important to management decisions. Several proxy indicators have been applied to core chronologies as highlighted above, however there may be up to 4000 years of environmental record remaining to be interpreted due to paucity in datable material down-core. Further, although the above mentioned work focused on salinity and water quality parameters in the bay over time, none address the specific history of seagrass distributions or the frequency of planktonic algal blooms in Florida Bay. In addition, while many studies have utilized paleoecological proxies, only a few have employed sediment geochemical parameters (Orem et al. 1999, Nelson et al. 2002), and in these cases sampling resolution was relatively low, limiting the interpretation of processes occurring on restricted temporal scales.

While understanding the historical environment of Florida Bay is integral to accurate planning of restoration efforts, the system as it functions today must be characterized so that alterations during the process of restoration may be recognized. Ecological studies are of course numerous, and water quality monitoring has been a focus over the previous two decades (Boyer et al. 1997, 1999, Rudnick et al. 1999) as efforts continue to gain insight into observed ecosystem-wide changes (Fourqurean and Robblee 1999). However, research aimed at understanding nutrient cycling from an isotopic perspective is isolated. Studies of seasonal and spatial variability in isotopic composition and elemental content of seagrasses in Florida Bay suggest significant variations not only in productivity and fractionation in the seagrasses themselves, but also in nutrient source inputs and in seasonal processing through microbially mediated nitrogen cycling

reactions. In addition, there is defined seasonal variability in carbon isotopic composition which is dependent upon growth rate and possibly freshwater dissolved inorganic carbon delivery (Anderson and Fourqurean 2003, Fourqurean et al. 2005). Behringer and Butler (2006) examined carbon sources in Florida Bay hardbottom communities, citing the benthic macroalgal community as the dominant source of secondary production to these ecosystems rather than seagrass or phytoplankton. Yet, while seasonal isotopic changes in these dominant benthic producers have been well constrained in efforts to relate geochemical indicators to surface nutrient processes, very little has been done with regards to understanding isotopic changes in water column communities within Florida Bay. Studies by Williams et al. (2009) determined that Florida Bay phytoplankton biomass is dominated by pico- and nano-plankton and cyanobacteria are the main bloom-forming group in the bay, confirming previous efforts (Phlips et al. 1995, 1999; Lavrentyev et al. 1998). However, Maie et al. (2005) suggested that much of the pelagic organic matter is not associated with living microbial (bacteria and algae) biomass but is detritus originating from seagrass and algae which is in some environments augmented by periodic influx of organic matter from the Everglades. Additionally, Xu and Jaffé (2007) reported significant differences in POM composition between wet and dry seasons in Florida Bay as indicated by a suite of organic biomarkers. While wet season POM was dominated by marine phytoplankton, dry season samples demonstrated more terrestrial influence reflecting the magnitude of marine primary productivity during wet season nutrient inputs (Xu and Jaffé 2007). These POM studies suggest high levels of variability in composition of water column particulate organics. Further investigation of this variability applying stable isotopic tools to clarify seasonal patterns, perhaps relating

OM sources to nutrient processes, might further understanding of the system as a whole, adding an additional component to previously developed and ongoing geochemical monitoring.

1.1.2 Florida Keys Reef Tract, Florida Keys National Marine Sanctuary

The Florida Keys Reef Tract consists of a series of coral reefs broken by shallow channels, separated from shore by 5 to 8 km of water ranging in depth from 3 to 10 m. With the exception of reef systems surrounding Bermuda, the reefs of the Florida Keys represent some the northernmost latitudinal limits of Caribbean coral species. These communities have moderate percent areal cover (10-50%) of hard and soft corals, benthic algae, and sponges (Leichter et al. 2008). Reef crests lie at 3 to 10 m depth, with forereefs sloping to 30 to 35 m depth, becoming gradually discontinuous until they are semi-isolated patches on sand. Seaward of the reef tract, the bottom slopes such that depth increases by 10-20 m per km until reaching the edge of the Florida Shelf, where slope angle increases into the deep channel of the Florida Straits (depths of 800-1200 m between 70 and 100 km offshore). The Florida Current is typically located between 10 and 40 km seaward of the reef tract flowing between 0.5 and 1.5 m s⁻¹ to the NE (Leichter et al. 2008). In terms of hydrodynamic regime, the reef tract is exposed to the episodic input of nutrients from upwelling and associated uplift of isotherms by frontal eddies of the Florida Current and internal waves acting at tidal frequencies (Leichter et al. 2003). High levels of both inorganic nitrogen and phosphorus below the thermocline point to the potential for the offshore nutrient pool to be a significant source of nutrients during these episodic upwelling events. In addition, the exchange of water through tidal channels

connecting the Gulf of Mexico/Florida Bay to the Atlantic Ocean is an important feature of regional circulation, carrying a net outflow of nutrients from Florida Bay, which may then be advected toward the reef tract (Smith 1998, Gibson et al. 2008).

In the last three decades, human activities in the Florida Keys have almost doubled, with concomitant increases in waste/nutrient inputs, thus a large body of recent research has investigated the impact of nutrient releases on the sensitive coral ecosystem of the reef tract (Lapointe and Clark 1992, Lapointe et al. 2004, Ward-Paige et al. 2005). Results are contradictory, with several investigators citing anthropogenic waste having a severe impact, particularly based on arbitrarily assigned isotopic indicator points (Lapointe et al. 2004 Ward-Paige et al. 2005), while others maintain that upwelling events related to internal tidal bores supply over 30 times more phosphorus and nitrogen than all estimated anthropogenic inputs from the Keys (Szmant and Forrester 1996, Leichter et al. 2003). Recent studies of the isotopic composition of the regionally dominant seagrass, *Thalassia testudinum*, also contradict the pervasiveness of anthropogenic nutrient disturbance, with seagrass tissues exhibiting $\delta^{15}\text{N}$ values ranging between -0.5 and + 4.0‰ (Anderson and Fourqurean 2003, Fourqurean et al. 2005), generally lower than those commonly associated with anthropogenic waste nutrient pollution. Further, the extensive investigation of Lamb (2006) into reef nutrient dynamics failed to demonstrate isotopic evidence of significant anthropogenic contamination in particulate organic material along numerous inshore to offshore transects along the Florida Keys Reef Tract (Lamb and Swart 2008). Similar to Florida Bay, while much work has been done in the Florida Keys National Marine Sanctuary investigating the isotopic composition of benthic macrophyte and macroalgal

communities (Lapointe and Clark 1992, Lapointe et al. 2004, Anderson and Fourqurean 2003, Fourqurean 2005), very little has been done to investigate spatial and temporal variability in the isotopic composition of water column particulate organic material (Lamb and Swart 2008). The present study builds upon the work of Lamb (2006), further clarifying nutrient and particulate sources in the nearshore environment of the Florida Keys Reef Tract, and adds to our understanding of nutrient processes in the South Florida coastal zone.

1.1.3 Stable Isotopes of Carbon and Nitrogen

Nitrogen and carbon isotopic ratios ($^{15}\text{N}/^{14}\text{N}$ and $^{13}\text{C}/^{12}\text{C}$) in sedimentary and suspended particulate organic matter, precipitating inorganic material, and residual water column dissolved pools are presently being explored as unique natural recorders of marine nutrient cycling, biogeochemistry, and primary productivity (Wu et al. 1997, Altabet et al. 1999, Waser et al. 2000, and others). $\delta^{13}\text{C}^*$ signatures have been widely used in both lacustrine and marine sediments not only as indicators of organic matter source, but also as indicators of enhanced aquatic productivity (McKenzie 1985, Calvert et al. 1992, Shamesh et al. 1993, Minoura et al. 1997, Schubert and Calvert 2001). $\delta^{13}\text{C}$ signature may be used as a productivity indicator because photosynthetic discrimination processes preferentially incorporate ^{12}C , thus the resultant organic matter is relatively “depleted” in terms of ^{13}C , leaving the dissolved carbon pool in the photic zone and subsequently generated organic carbon enriched in ^{13}C (McKenzie 1985, Hollander and

$$^* \delta^{13}\text{C} (\text{‰}) = [(^{13}\text{C}/^{12}\text{C}_{\text{sample}} / ^{13}\text{C}/^{12}\text{C}_{\text{standard}}) - 1] * 1000$$

$$\delta^{15}\text{N} (\text{‰}) = [(^{15}\text{N}/^{14}\text{N}_{\text{sample}} / ^{15}\text{N}/^{14}\text{N}_{\text{standard}}) - 1] * 1000$$

McKenzie 1991). During periods of high or increased primary productivity, photic zone depletion of the light isotope may force decreases in discrimination, increasing the relative proportion of ^{13}C that is fixed (Brenner et al. 1998, Muller and Voss 1999). Further, rapid rates of primary production may deplete the water column of the available free aqueous CO_2 , and some aquatic primary producers may increasingly rely on enriched bicarbonate (HCO_3^-) as a carbon source consequently producing ^{13}C -enriched organic matter (Fogel et al. 1992, Eadie et al. 1994, Muller and Voss 1999).

More recently, $\delta^{15}\text{N}$ values have become a complimentary proxy in both modern and paleoceanographic settings (Calvert et al. 1992, Francois et al. 1992, Teranes and Bernasconi 2000). Nitrogen isotopes behave much like carbon isotopes during biotic uptake and utilization in the euphotic zone. In non-limiting environments, lighter ^{14}N is preferentially incorporated in plant biomass and is subsequently recycled in higher trophic levels, buried, or released through denitrification processes as non-bioavailable N_2 gas. More commonly, nitrogen is in limited supply dependent on seasonal upwelling and/or discharge. Studies show that the $\delta^{15}\text{N}$ of organic matter is inversely related to the degree of surface water nitrate (NO_3^-) consumption where N is a limiting nutrient. As the NO_3^- concentrations progressively decline the residual NO_3^- pool becomes isotopically enriched and is then exploited to support autotrophic productivity (Wu et al. 1997, Altabet et al. 1999, Sigman et al. 2000, Waser et al. 2000, Mahaffey et al. 2003, Mahaffey et al. 2004). Many researchers then interpret enriched $\delta^{15}\text{N}$ values as indicative of high productivity, or more specifically high surface nitrate utilization (Wainright and Fry 1994, Wu et al. 1997, Altabet et al. 1999, Rolff 2000, Waser et al. 2000).

In the last decade, many studies have shown that combined interpretations of the carbon and nitrogen isotopic systems generate a more complete picture of productivity levels and nutrient utilization (Ostrom et al. 1997, Brenner et al. 1999, Muller and Voss 1999, Struck et al. 2001, Schubert and Calvert 2001). When both carbon and nitrogen are limiting, their isotopic signatures can be expected to show a positively correlated enrichment trend with increasing productivity. Alternatively, an inverse relationship will be evident between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ trends should one of the nutrients be abundant while the other is limiting under increasing productivity (Schubert and Calvert 2001). Supporting $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values with C:N:P (Redfield ratios) from organic matter can further clarify nutrient limitation trends and primary productivity interpretations (Anderson and Fourqurean 2003). However, interpreting stable isotope ratios in terms of productivity is not without caveat. Nitrogen isotopes present a particular problem, especially in systems where phosphorus is more limiting than nitrogen, as in many lacustrine and some marine environments, for example the carbonate based system of coastal Florida (Fourqurean and Zieman 1992, Millero et al. 2001). In these environments, only part of the ambient dissolved inorganic nitrogen (DIN) pool is consumed and the residual DIN isotopic composition may never be appreciably altered. Under these conditions, primary productivity cannot be inferred from the $\delta^{15}\text{N}$ of organic matter in the system, because other factors often more strongly influence the N-isotopic signal (Teranes and Bernasconi 2000). For example, the concentration of DIN can be more variable than DIC concentrations at the surface, which in turn can cause variations in the $\delta^{15}\text{N}$ of the N-source. In addition, variations in the dissolved N-species may further convolute this problem. Ammonium (NH_4^+) may be utilized by autotrophs as an

alternative to NO_3^- , however the isotopic signature of ammonium can vary from extremely depleted $\delta^{15}\text{N}$ values in excretion products to enriched values if produced through ammonification of primary organic matter (Ostrom et al 1997). Further, dissolved NH_4^+ is also more highly fractionated during biotic uptake than NO_3^- (fractionation (ϵ) = 6.5-9.0‰ in NH_4^+ whereas ϵ = 2–5‰ in NO_3^- ; Waser et al. 2000). This difference in fraction might lead to differential residual ^{15}N enrichment between NH_4^+ and NO_3^- at similar uptake rates, complicating assumptions that enrichment signatures are indicative of NO_3^- dependence/limitation in the system being examined. In addition, denitrification operating in anoxic basins and anoxic zones within the sediment can also be expected to enrich the dissolved N pool in ^{15}N , whereas N-fixation inputs of relatively depleted $\delta^{15}\text{N}$ may offset the expected enrichment, disguising the productivity signature (Eadie et al. 1994, Hodell and Schelske 1998).

Shifts in autotrophic species composition or addition of heterotrophs can also influence the $\delta^{15}\text{N}$ composition of sedimenting organic matter. The organic matter $\delta^{15}\text{N}$ composition is even more affected by shifts favoring diazotrophic N-fixing species, which generate delta values near the atmospheric standard, 0‰ (Eadie et al. 1994, Hodell and Schelske 1998, Schubert and Calvert 2001). Understanding speciation changes may be particularly important in interpreting seasonal variability in planktonic isotopic signatures, as the species composition of the community varies considerably over seasonal cycles with changing nutrient availability, and also with a variety of other environmental parameters including temperature, salinity, irradiance, etc. (Boyer et al. 1997). Additionally, changes in trophic structure may also influence the both $\delta^{15}\text{N}$ and to

a lesser extent the $\delta^{13}\text{C}$ of organic matter, as it is well known that $\delta^{15}\text{N}$ increases by 3-4‰ and $\delta^{13}\text{C}$ increases by about 1‰ per trophic transfer (Peterson and Fry 1987). Isotopic variation will also be introduced by variations in the proportions of macrophytes versus algae contributing to sedimentary organic matter, as well as terrestrial versus marine inputs – all of which show significant differences in both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures (Brenner et al. 1999, Muller and Voss 1999). Further complication of terrestrial versus marine isotopic signals has been highlighted by recent work examining isotopic responses in wetland plant tissues with changes in water level, hydro-period, precipitation, and salinity stress. Wide variations in the isotopic composition of wetland plants and trees can be induced by localized environmental conditions because changes in water use efficiency can alter carbon assimilation rates and isotopic discrimination associated with photosynthesis (Anderson et al. 2005, Ewe and Sternberg 2002, 2003). Anoxia in saturated root zones can induce decreases in stomatal conductance, causing isotopic enrichment (Ewe and Sternberg, 2002, 2003, Anderson et al. 2005). In this manner then, seasonal changes in precipitation and transitions through the drought cycle can be expected to significantly alter the isotopic composition of wetland macrophyte detritus entering the coastal zone. Anderson et al. (2005) showed a positive correlation between precipitation and pond cypress isotopic composition in the freshwater Everglades, thus longer hydro-period in the upstream Everglades may lead to isotopic enrichment in particulate detritus. Salinity stress, though seeming to be the opposite of water stress associated with increases in freshwater hydro-period, may also induce decreases in stomatal conductance and ensuing isotopic enrichment (Anderson et al. 2005). The $\delta^{13}\text{C}$ enrichment under both water stress cases is significant enough to

generate confusion between terrestrial and marine isotopic signals, as both pond cypress under freshwater stress and bald cypress under salinity stress exhibited cellulose $\delta^{13}\text{C}$ values between -20 and -22‰; values that are conventionally considered diagnostic of planktonic marine organic material.

Before C and N isotopic signals can be interpreted with confidence in terms of paleoproductivity and nutrient limitation in time-series data sets or core stratigraphy, processes as they occur locally in modern environments must be understood. As always, the present is the key to the past and examining modern analogues is important for calibrating development in a system over time, which will lead to improved reconstructions.

1.2 RATIONALE

In the case of Florida Bay, stable isotopic signatures recorded in both sedimentary and suspended organic matter represent useful tools to gain understanding of carbon and nitrogen cycling in a shallow carbonate estuary. Although nutrient budgets have been constructed for Florida Bay, and the flux magnitudes of internal N-cycling chemical processes are the subject of ongoing work (Rudnick et al. 1999, Nagel 2004, Cornwell et al. unpublished data). Thus far, the N dynamics within the system have not been well constrained in terms of changing availability of DIN species and their relative utilization by both benthic and planktonic autotrophs. $\delta^{15}\text{N}$ has not been measured on a comprehensive level in POM in the system and no efforts have yet been made to clarify finer points in the N-cycle of Florida Bay using N stable isotopes. Although there have been studies applying $\delta^{13}\text{C}$ values to track organic carbon sources in particulate organic

carbon (POM) delivery to the bay via Taylor Slough and Shark River Slough (Mead 2004), the N isotopes in this freshwater POM discharge have not been examined, yet this material may represent a significant component of the Florida Bay N-cycle. Further, isotopic studies of the estuarine food web have been completed (Zieman et al. 1984, Harrigan et al. 1989); however, analysis of spatial and temporal variations C and N isotopic composition of organic matter related to seasonal productivity changes has been limited to the regionally dominant seagrass, *Thalassia testudinum* (Anderson and Fourqurean 2003). Three years of quarterly $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements on *Thalassia*, collected from sites on both the ocean and bay sides of the Florida Keys, show that the seasonal variability observed in seagrass productivity is also present in the isotopic signals of both N and C. However, relationships between the two isotopic systems vary on both spatial and temporal scales, potentially demonstrating nutrient decoupling between the driving mechanisms behind variability in C and N isotopic signatures (Anderson and Fourqurean 2003).

The seagrass community is only one component of the local N-cycle. The phytoplankton/POM isotopic signal is a significant missing element that has yet to be documented. Due to the nature of the planktonic community - high population turn-over rates, variable transport mechanisms within the water column, and the tight coupling between both phytoplankton productivity, speciation, and seasonal environmental changes - $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signals are expected to exhibit more spatial and temporal variability than the macrophytes. Additionally, rooted aquatic vegetation primarily responds to nutrient concentrations available in pore water, whereas the pelagic community reacts directly to surface water quality (Fourqurean et al. 1992). For the same

reasons, the phytoplankton may also show pronounced responses to changes in nutrient source and availability much more quickly than the macrophyte community, thus the suspended community might represent a better tool for constraining seasonality and spatial variability in N-cycling.

Short term seasonal variability has been identified in benthic macrophyte communities of a magnitude equal to long term fluctuations observed in geologic records for the Phanerozoic. In order to apply stable isotope systematics as a tool to understand and predict future change in the system it is important to first establish modern baseline data, particularly in the context of biological productivity, and the extent of natural/seasonal variations before geologic records can be interpreted. As such, the purpose of this work was to more completely constrain modern C and N cycling in Florida Bay and the adjacent Florida Keys near-shore reef system in terms of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. In particular, variability in carbon and nitrogen isotopic values was investigated. Findings in the modern environment will then be applied to the sedimentary record of Florida Bay, possibly shedding light on past nutrient cycling, organic matter sources, and paleoproductivity in the bay and adjacent systems.

1.3 HYPOTHESES

The work described here is based on the following set of hypotheses:

Hypothesis 1: Organic matter sources comprising the total pool of particulate organic material in South Florida coastal ecosystems are variable on a seasonal basis, reflecting productivity changes in various biological components of the system, wet-dry season

cycles in freshwater flow delivery, and seasonal climate patterns (wind, storm forcing, etc.).

Hypothesis 2: Patterns in the spatial and temporal variability of particulate organic material stable isotopic composition are related to seasonal changes in nutrient availability.

Hypothesis 3: Spatial variability evident in the isotopic compositions of both particulate organic material and benthic seagrasses is preserved in sedimentary organic material.

1.4 OBJECTIVES

To approach the purpose and set of hypotheses stated above, the following research objectives were addressed:

- 1.** A size-fractionated, seasonal particulate organic matter isotopic time series will be generated broadly separating zooplankton, larger phytoplankton, and smaller phytoplankton/bacterial components for ten sites within Florida Bay and along the Florida Reef Tract in an effort to understand autochthonous particulate inputs and cycles to the coastal system.
- 2.** Spatial and temporal variability in the POM isotopic time series will be compared to the existing and continuing data set of the isotopic composition of seagrass, and to available data sets of ambient DIN availability to assess relationships among parameters.

4. The sedimentary record of Florida Bay will be interpreted in terms of variation in organic matter source, paleoproductivity, relative nutrient utilization, and changing nutrient sources over the geologic history of Florida Bay using organic matter $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements from dated sediment cores.

1.5 DISSERTATION ORGANIZATION

Chapter 1 provides background information for this study. General descriptions of carbon and nitrogen isotope theory are given, followed by an introduction to the current state of applicable research in both Florida Bay and along the Florida Reef Tract.

Chapters 2 through 4 represent the main body of research conducted in the present study, examining components of the isotopic systematics of the South Florida marine system at a variety of time scales. At the process level, organic matter stable isotopic values were applied to assess nutrient acquisition mechanisms in a single transient cyanobacterial bloom event (Chapter 2). From a longer term seasonal point of view, isotopic values demonstrated a high level of spatial and temporal variability in particulate organic matter, supporting previous work characterizing the significance of hydrodynamic regime as a control on coastal processes (Chapter 3). Increasing the scale further, geochemical data was utilized to assess organic matter source and identify markers of disturbance in the last century (Chapter 4).

Chapter 5 presents a synthesis of results showing the relationships between isotopic records across the time-scales examined and outlines possible future research directions.

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CHAPTER 2

SPATIAL VARIABILITY IN FLORIDA BAY PARTICULATE ORGANIC MATTER COMPOSITION: COMBINING FLOW CYTOMETRY WITH STABLE ISOTOPE ANALYSES

2.1 ABSTRACT

Long term management plans for restoration of natural flow conditions through the Everglades increase the importance of understanding potential nutrient impacts of increased freshwater delivery on Florida Bay biogeochemistry. Planktonic communities respond quickly to changes in water quality, thus spatial variability in community composition and relationships to nutrient parameters must be understood in order to evaluate future downstream impacts of modifications to Everglades hydrology. Here are presented initial results combining flow cytometry analyses of phytoplankton and bacterial populations (0.1-50 μm size fraction) with measurements of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ composition and dissolved inorganic nutrient concentrations to explore proxies for planktonic species assemblage compositions and nutrient cycling. Particulate organic material in the 0.1-50 μm size fraction was collected from five stations in Northeastern and Western Florida Bay to characterize spatial variability in species assemblage and stable isotopic composition. A dense bloom of the picocyanobacterium, *Synechococcus elongatus*, was observed at Western Florida Bay sites. Smaller *Synechococcus* sp. were present at Northeast sites in much lower abundance. Bacteria and detrital particles were also more abundant at Western Florida Bay stations than in the northeast region. The highest abundance of detritus occurred at Trout Creek, which receives freshwater discharge from the Everglades through Taylor Slough. In terms of nutrient availability and stable isotopic values, the *S. elongatus* population in the Western bay corresponded to low DIN ($0.5 \mu\text{M NH}_4^+$; $0.2 \mu\text{M NO}_3^-$) concentrations and depleted $\delta^{15}\text{N}$ signatures ranging from +0.3 to +0.8‰, suggesting that the bloom supported high productivity

levels through N_2 -fixation. The $\delta^{15}N$ values from the Northeast bay were more enriched (+2.0 to +3.0‰), characteristic of N-recycling. The $\delta^{13}C$ values were similar for all marine Florida Bay stations, ranging from -17.6 to -14.4‰, yet were depleted at the mangrove ecotone station, Trout Creek (-25.5 to -22.3‰). The difference in the isotopic values reflects differences in carbon sources. These findings imply that variations in resource availability and nutrient sources exert significant control over planktonic community composition, which is reflected by stable isotopic signatures.

2.2 INTRODUCTION

Florida Bay has been influenced by changes in the timing and volume of freshwater flow from the Everglades in the last half century as a result of extensive modification of the natural discharge patterns by water management infrastructure (Davis & Ogden 1994, Rudnick et al. 1999). This has prompted researchers to explore the extent to which salinity levels in the bay have been affected by these changes (Huvane, 2002). Further, it is hypothesized that human alteration of the Everglades watershed in the last century facilitating agriculture and urbanization may have increased nutrient loads to downstream Florida Bay leading to unknown impacts on the ecosystem (Fourqurean et al. 1993, Boyer et al. 1999). In the same time frame, biotic and water quality parameters have changed significantly (Lapointe et al. 2002). Historically, Florida Bay was a shallow, optically clear lagoon characterized by low nutrient levels and populated by abundant seagrass communities. However, in recent decades significant declines have been observed in water clarity, hypersaline conditions have periodically developed during

summer months (Boyer et al. 1999), and widespread die-off events have occurred in the seagrass communities (Zieman et al. 1989, Fourqurean et al. 1993), coincident with phytoplankton blooms (Robblee et al. 1991, Butler et al. 1995, Phlips & Badylak 1996). Causal mechanisms behind this shift in biotic communities remain the focus of ongoing study; however, the trigger for phytoplankton blooms is not fully understood (Richardson & Zimba 2002).

Given long term management plans to restore more natural flow conditions through the Everglades, a key concern is the extent to which nutrients passing through or originating from the Everglades impact Florida Bay. Restored flows may alter the forms, amount, and temporal distribution of dissolved nutrients delivered to the bay. Planktonic communities respond quickly due to high population turnover rates and the tight association with water quality. In turn, the structure of these planktonic communities can have significant effects on biogeochemical cycles of nutrients (Lavrentyev et al. 1998). Yet, while much attention in Florida Bay has focused on changes in seagrass abundance and distribution (Zieman et al. 1989, Anderson & Fourqurean 2003, Fourqurean et al. 2005), aspects of the composition and community dynamics of particulate organic matter (POM) remain poorly understood.

Several studies have taken steps toward characterizing Florida Bay's phytoplankton community applying cell counting and pigment extraction techniques, demonstrating the bay is extremely variable in terms of both species diversity and biomass (Phlips & Badylak 1996, Lavrentyev et al. 1998, Phlips et al. 1999, Richardson & Zimba, 2002). Cyanobacteria, diatoms, and dinoflagellates have been identified as dominant organisms (Phlips & Badylak 1996), but relative population abundances of

several species in each group vary widely both spatially and temporally (Richardson & Zimba, 2002). Lavrentyev et al. (1998) characterized the microbial plankton community with respect to resource limitation with a short term bay-wide survey, dividing the bay into three regions based on community structure and elemental stoichiometry. The North-central region of Florida Bay contained the highest cyanobacteria abundance (Lavrentyev et al. 1998). Physical restriction of tidal exchange between this interior zone and the surrounding oceanic environments enhances potential for accumulation of cyanobacterial biomass by increasing water residence times, while euryhaline cyanobacteria species are unaffected by periodic hypersaline conditions (Phlips et al. 1999).

Understanding of the biogeochemical connections between nutrient resources and population dynamics within the phytoplankton and bacterial components of POM is conspicuously absent in the literature. Isotopic-enrichment tracer techniques assessing utilization of organic nitrogen (N) substrates during a cyanobacteria bloom event has shown in one instance that cyanobacterial blooms in Central Florida Bay are associated with high dissolved organic nutrient availability, whereas areas dominated by microflagellate and diatom communities are dependent upon inorganic nutrient resources (Glibert et al. 2004). The utility of natural isotopic abundance measurements to assess biogeochemical coupling between nutrient resources and planktonic communities has not been well explored. It is possible that bulk samples of the 0.1-50 μm POM fraction collected at sites characterized by different water quality parameters and nutrient availability will have distinct isotopic fingerprints based on species composition

differences, or may reflect relative nutrient utilization between varying N-sources (nitrate (NO_3^-) versus ammonium (NH_4^+)) and nitrogen versus carbon limitation.

Here I present initial results combining flow cytometry analyses of phytoplankton and bacterial populations with natural abundance carbon and nitrogen isotopic signatures to explore proxies for biotic assemblage characteristics. Flow cytometry represents an advantage over traditional fluorescence microscopy and HPLC pigment analysis in that it allows efficient and objective analysis of large numbers of particles, with the facility to distinguish organic living and non-living particles (Moreira-Turcq & Martin 1998). However, limitations in the numbers of pigments analyzed restrict taxonomic resolution as compared to other methods (Veldhuis & Kraay 2000). Procedures coupling flow cytometry sorters with pyrolysis mass spectrometry for in-line analysis are currently under development (Minor & Nallanthamby 2004; Pel et al. 2004), however at present sorted sample volumes are insufficient to perform $\delta^{15}\text{N}$ analyses, and isotopic values can only be obtained for $\delta^{13}\text{C}$.

In this approach, flow cytometry is used to distinguish bacteria, cyanobacteria, eukaryotic phytoplankton, and detritus, allowing a broad view of POM composition at endmember locations in terms of Florida Bay nutrient and salinity gradients. The composition of POM is then compared with isotopic measurements. Further characterization and exploration of size-fractionated isotopic signatures advances understanding of phytoplankton, microbial, and biogeochemical dynamics in the system.

2.3 METHODS

2.3.1 Setting

Florida Bay consists of a series of shallow basins (<3 m depth) separated hydrologically by a network of subtidal mudbanks and mangrove islands which restrict water mixing between basins and attenuate both tidal amplitude and current. Freshwater runoff, comparatively rich in dissolved inorganic nitrogen (DIN) and poor in soluble reactive phosphorus (SRP), enters this hydrologically complex system primarily in Northeastern Florida Bay through the Taylor Slough and the C-111 basin. Saline ocean water, comparatively depleted in DIN and enriched in SRP, enters across the western boundary with the Gulf of Mexico and through numerous tidal channels crossing the Florida Keys (Boyer et al. 1999). Interaction between these inflows and limitations on the bay's mixing regime serve to generate gradients in both salinity and nutrient availability across the bay. Salinity increases from the freshwater-affected northeastern region to the south and west to reach marine strength (36‰), with seasonal periods of hypersalinity (40-80‰) in restricted interior basins (Boyer et al. 1999). Nutrient gradients are evident in changing DIN:SRP ratios, which are considered an index of phytoplankton nutrient limitation, from northeast to southwest Florida Bay (Boyer et al. 1999). Long-term monitoring revealed little seasonality in consistently high DIN:SRP ratios in the eastern bay, indicating potentially continuous phosphorus (P) limitation (Boyer et al. 1999, Fourqurean et al. 1993). Western Florida Bay DIN:SRP ratios are over three times lower and more variable than those in the northeastern region, implying fluctuations between N and P limitation, due not only to lower DIN concentrations in the

western bay region than in the east, but also because SRP periodically supplied through mixing from the Gulf of Mexico (Boyer et al. 1999).

2.3.2 Sampling Locations and Collection

In November 2003, a “snapshot” of samples was collected at geographic end-member sites in the northeastern and western Florida Bay (Figure 2.1). Trout Creek (Station 5) represented a freshwater discharge influenced northeastern site (salinity 4.2‰), while Duck Key (Station 4) and South Nest Key (Station 3) were marine northeast Florida Bay sites (salinity 24.5‰). Ninemile Bank (Station 2) and Sprigger Bank (Station 1) were representative of full seawater salinity western Florida Bay

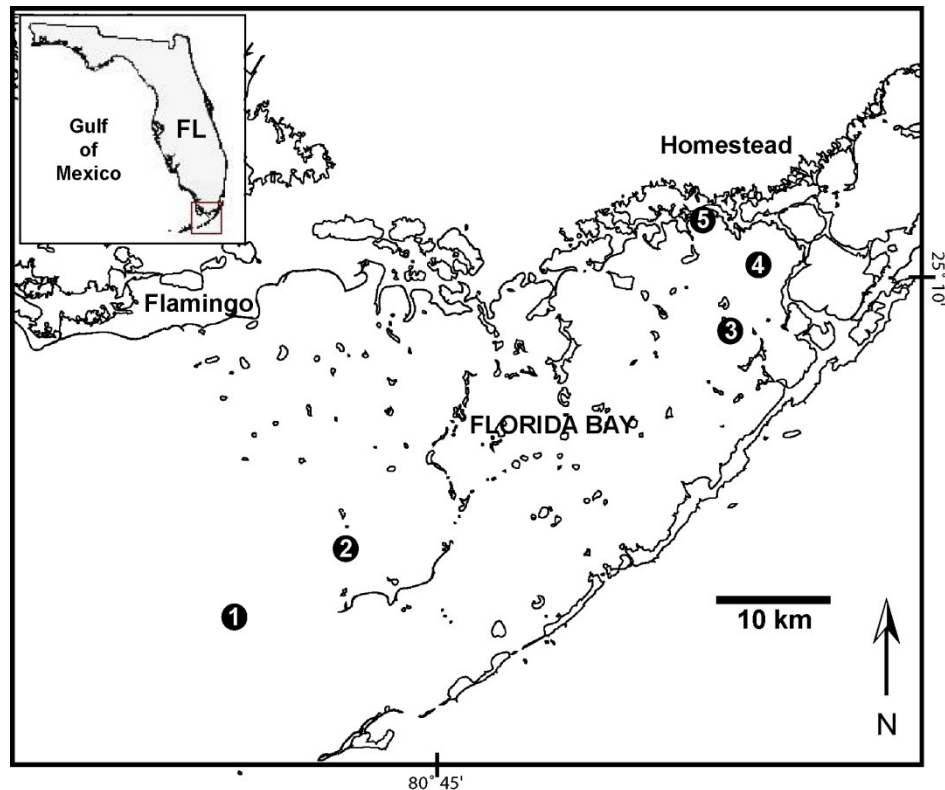


Figure 2.1 Map of Florida Bay, showing sampling locations in Western Florida Bay at Sprigger Bank (1) and Ninemile Bank (2), in Northeastern Florida Bay at South Nest Key (3) and Duck Key (4), and near the Taylor Slough Everglades outflow at Trout Creek (5).

locations (salinity 35.5‰). Three sets of water samples were collected at each site after first passing through a 50 µm Nitex screen to exclude larger size classes of zooplankton, phytoplankton, and detritus. Two replicate samples were collected at each station and preserved with formalin (final conc. 1%) for cytometric analysis. Water samples for nutrient analyses (30 ml) were syringe filtered with 0.45µm GF/F Whatman filters. Finally, 1 L samples were collected for stable isotopic analysis of the 0.1-50 µm POM fraction. All samples were kept in the dark and refrigerated at 5°C until time of analysis, which occurred within 3 days of sample collection. Salinity was measured using a digital Orion Temp/Salinity Meter.

2.3.3 Flow Cytometry Analyses

Heterotrophic bacteria and phytoplankton in the 0.1-50 µm POM fraction were counted on a Becton Dickinson FACSort flow cytometer equipped with an argon laser (488 nm). For each particle, two light scatter (side angle light scatter and forward light scatter) and three fluorescence signals were recorded on a 4-decades log scale. All data were analyzed using Win MDI 2.8 (Trotter 2000) flow cytometric analysis software to define populations by logical gating and generate plots illustrating 50 000 events (particle detections).

A DNA staining procedure was used to enumerate heterotrophic bacteria (Marie et al. 1997). A 500 µL sample aliquot was incubated with 25 µL RNAase (0.1 g L^{-1} , 1:1 mixture of RNAase A & B) for 30 minutes at 37°C, followed by the addition of 20 µL of SYBR Green I staining (10^{-5} dilution of commercial stock, Molecular Probes, Eugene, OR) in the presence of 30 mM potassium citrate. SYBR DNA fluorescence was recorded

in both the green FL1 (535 ± 15 nm) and red FL3 (>650 nm) fluorescence channels, DNA clusters of bacteria were counted by logical gating from both FL1 vs FL3 and SSC vs FL1 dot plots, and histograms with gate borders set to minima in population frequency distribution. Measured sample volumes for estimates of bacterial abundance (cells ml^{-1}) were calculated from measurement times (30 seconds) based on weight calibration of flow rates ($1 \mu\text{l s}^{-1}$; Jochem 2001).

For bulk phytoplankton samples, 1 ml of each replicate sample was analyzed without staining, as phytoplankton pigments exhibit detectable autofluorescence following laser excitation (Hofstraat et al. 1994). Phytoplankton populations were differentiated using chlorophyll autofluorescence, detected in the red FL3 (>650 nm) fluorescence channel, phycoerythrin autofluorescence, detected in the orange FL2 (575 ± 25 nm) fluorescence channel, and side angle light scatter was measured (SSC channel) for proxy analysis of relative cell size. Cell concentrations were calculated based on measurement times (150 seconds) and weight-calibrated flow rates.

2.3.4 Isotopic Analyses

Water samples (1L) were vacuum-filtered through Whatman Anodisc membrane filters ($0.1 \mu\text{m}$ pore size). These filters are aluminum oxide matrix, and thus do not influence carbon and nitrogen stable isotope signatures (Bertoni, 1997). Filters were oven dried (70°C) and powdered. Powdered filter samples were analyzed following standard Elemental Analyzer Isotope Ratio Mass Spectrometry (EA-IRMS) methods on a Finnigan MAT Delta C Isotope Ratio Mass Spectrometer at the Stable Isotope Laboratory of the Southeast Environmental Research Center. $\delta^{13}\text{C}$ analyses were conducted after

acidifying vials with approximately 5ml 1N HCl for carbonate removal. $\delta^{15}\text{N}$ analyses were conducted on raw filter material. Reproducibility of nitrogen isotope analyses was $\pm 0.2\text{‰}$, while carbon reproducibility was $\pm 0.05\text{‰}$, based on duplicate analyses of both samples and multiple internal laboratory standards.. All isotopic values are reported using standard delta (δ) notation:

$$\delta = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000 \quad (\text{Eq. 1})$$

Where R is the isotopic ratio, i.e. $^{15}\text{N}/^{14}\text{N}$ or $^{13}\text{C}/^{12}\text{C}$ in either sample or standard.

2.3.5 Nutrient Analyses

Surface water filtrates from each site were analyzed for nitrate + nitrite (NO_x^-), nitrite (NO_2^-), ammonium (NH_4^+), and SRP with an Alpkem model RFA 300 water autoanalyzer set to 4 channel simultaneous flow. Nitrate (NO_3^-) concentrations were calculated as $\text{NO}_x^- - \text{NO}_2^-$. These samples were compared to long term water quality data sets provided by the SERC-FIU Water Quality Monitoring Network.

2.4 RESULTS

Eukaryotic algae (EUK) and four distinct populations of cyanobacteria (numbered 1-4) were differentiated through logical gating of bivariate flow cytometry analysis plots (Figure 2.2). Each point on the individual plots represents a single particle detection, thus darker areas indicate higher particle densities. Groups of eukaryotic algae and cyanobacteria are shown within ellipses because they are difficult to distinguish visually in monochromatic plots. Spatial variability in assemblage and population abundance is

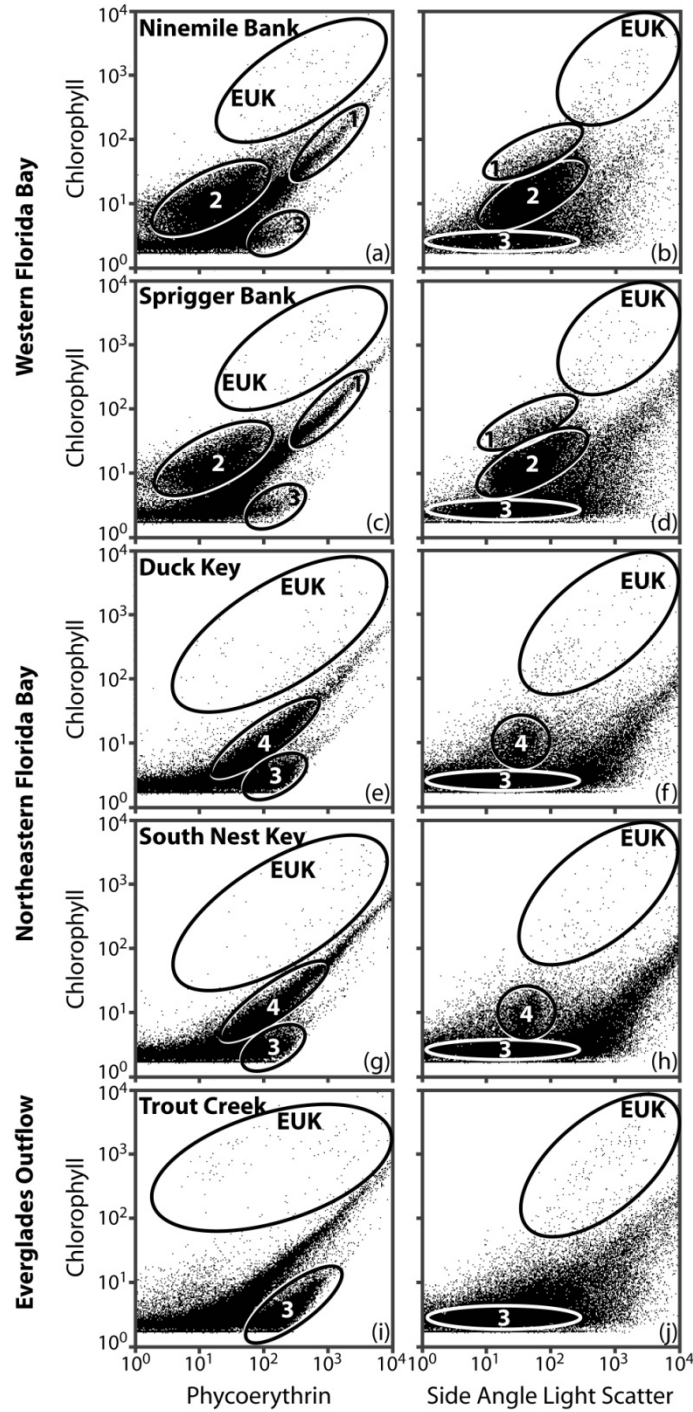


Figure 2.2 Flow cytometry analyses of Florida Bay phytoplankton collected at five sampling locations in Western (a-d) and Northeastern (e-h) Florida Bay, and proximal to the Everglades outflow (i-j). 50 000 events are displayed after acquisition in log mode. The left side plots from each site display phycoerythrin (FL2) against chlorophyll (FL3); the right side plots show Side Angle Light Scatter (relative cell-size proxy) with chlorophyll. All axes are on a 4 decade log scale. Eukaryotic algae (EUK) and 4 distinct cyanobacterial populations are shown (circled and numbered 1-4), as determined using logical gating between the plot pairs from each site. Particles not included in definable populations of cells are considered detrital particles.

Table 2.1 Mean and S.D. of phytoplankton and bacteria population abundances determined by logical gating (Win MDI; Trotter 1994-2000) for samples collected during the Nov. 2003 Florida Bay snapshot POM sampling. All values are cells ml⁻¹ * 10³

Site	Total Phytoplank.	Eukaryotes	Cyanobact. 1	<i>S. elongatus</i> * Cyanobact. 2	<i>Syn. sp.**</i> Cyanobact. 3	Cyanobact. 4	Detritus	Bacteria
Sprigger Bank	660.3 ± 65.2	1.7 ± 0.2	46.7 ± 1.1	532.9 ± 25.0	81.5 ± 40.3		627.6 ± 47.9	2058.1
Ninemile Bank	934.8 ± 87.8	3.5 ± 0.8	79.5 ± 13.9	801.9 ± 56.3	66.8 ± 22.2		655.1 ± 220.0	2412.1
South Nest Key	33.7 ± 5.5	0.8 ± 0.1			8.6 ± 3.9	32.1 ± 4.90	261.6 ± 59.6	854.1
Duck Key	166.6 ± 38.9	3.4 ± 0.4			80.0 ± 75.2	37.4 ± 11.3	245.9 ± 71.8	623.5
Trout Creek	520.7 ± 81.6	4.6 ± 1.8			522.0 ± 81.2		1157.0 ± 457.5	1431.8

**Synechococcus elongatus*.

***Synechococcus* sp.

evident (Table 2.1). The highest abundances were seen in the low chlorophyll, low phycoerythrin population, *Synechococcus elongatus* (Figure 2.2; Cyanobacteria 2), with $801.9 \pm 56.3 \times 10^3$ and $532.9 \pm 25.0 \times 10^3$ cells ml⁻¹ present only at the western Florida Bay sites (Ninemile Bank and Sprigger Bank, respectively). *S. elongatus* is known to form blooms in central and western Florida Bay (Lavrentyev et al. 1998; Philips et al. 1999, Glibert et al. 2004). A second population of *Synechococcus* sp, distinguished by higher phycoerythrin and a smaller size (Figure 2.2; Cyanobacteria 3), was present at all stations, but with higher densities at the northeastern sites and with highest abundance ($522.0 \pm 81.2 \times 10^3$ cells ml⁻¹) at Trout Creek. Cyanobacteria 4, similar in size to *S. elongatus*, but with higher phycoerythrin content, were present at much lower abundance at northeast Florida Bay sites ($32.1 \pm 4.90 \times 10^3$ cells ml⁻¹ at South Nest; $37.4 \pm 11.3 \times 10^3$ cells ml⁻¹ at Duck Key). Eukaryotic algae were present at all stations in very low abundance, with the largest population at the Trout Creek site ($4.6 \pm 1.8 \times 10^3$ cells ml⁻¹).

High abundances of autofluorescing detrital particles were evident at all stations (Table 2.1); however, the largest detrital signal occurred in the Everglades freshwater discharge exiting Taylor Slough at Trout Creek. The west Florida Bay stations had threefold higher detritus concentrations than the northeastern sites. Bacterial communities also differed spatially between western and northeastern Florida Bay (Figure 2.3). Up to five populations of bacteria exhibiting different DNA content were evident at all marine Florida Bay stations, but were less distinct at Trout Creek. Two additional populations with higher red fluorescence were abundant at western bay region, present at northeastern sites in much lower abundance; these may represent *Prochlorococcus* sp., or additional bacterial populations.

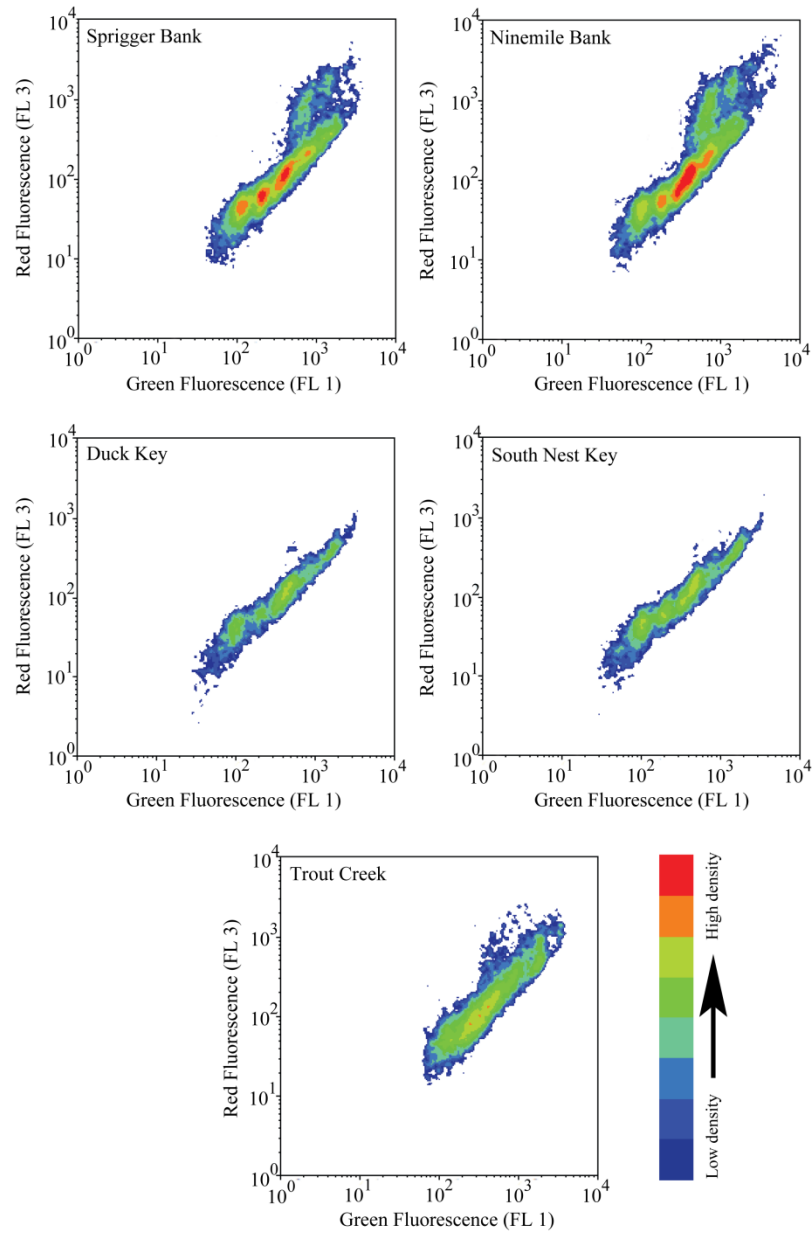


Figure 2.3 Flow cytometry analyses of November, 2003, Florida Bay surface water bacteria samples after DNA staining with SYBR Green. Green fluorescence (FL1) vs red fluorescence (FL3) are shown for all sites on a 4 decade log scale.

The maximum bacteria concentrations were measured at Ninemile Bank (2.412×10^6 cells ml^{-1}), while much lower bacteria concentrations were found at northeastern sites (0.623×10^6 cells ml^{-1} at Duck Key; 0.854×10^6 cells ml^{-1} at South Nest Key). Trout

Creek, in the mangrove ecotone, exhibited higher bacterial abundance than the open water northeast Florida Bay stations (Table 2.1).

Carbon and nitrogen isotopic signatures demonstrate differences between geographic endmembers of Florida Bay environmental gradients (Figure 2.4). The Trout Creek location exhibited the most depleted carbon values (-25.3‰ to -22.3‰), whereas the open water locations in both western and northeastern Florida Bay were slightly more enriched, ranging from -17.6‰ to -14.4‰. $\delta^{15}\text{N}$, however, differed between west and northeast Florida Bay. At northeastern sites, nitrogen isotopic signatures were +2.0‰ to +3.0‰, while more depleted values were evident at western bay stations, where a minimum $\delta^{15}\text{N}$ value of +0.3‰ was observed. The variation in POM nitrogen isotopic signal is coincident with a large difference in inorganic nitrogen concentrations between endmember locations (Figure 2.4). The western sites had over an order of magnitude lower ammonium (NH_4^+) concentrations (9.5 vs 0.5 μM NH_4^+ , northeast and west sites, respectively) and nearly an order of magnitude lower nitrate (NO_3^-) levels (1.2 vs 0.2 μM NO_3^- , northeast and west).

2.5 DISCUSSION

High spatial heterogeneity in the 0.1-50 μm POM fraction across Florida Bay was reflected by differences in community composition, relative significance of individual sub-populations, total phytoplankton and bacterial abundances, and detritus loads. These differences are not unexpected, as noted in previous studies of the Florida Bay planktonic community (Phlips & Badylak, 1996, Philips et al. 1999, Lavrentyev et al. 1998, Glibert et

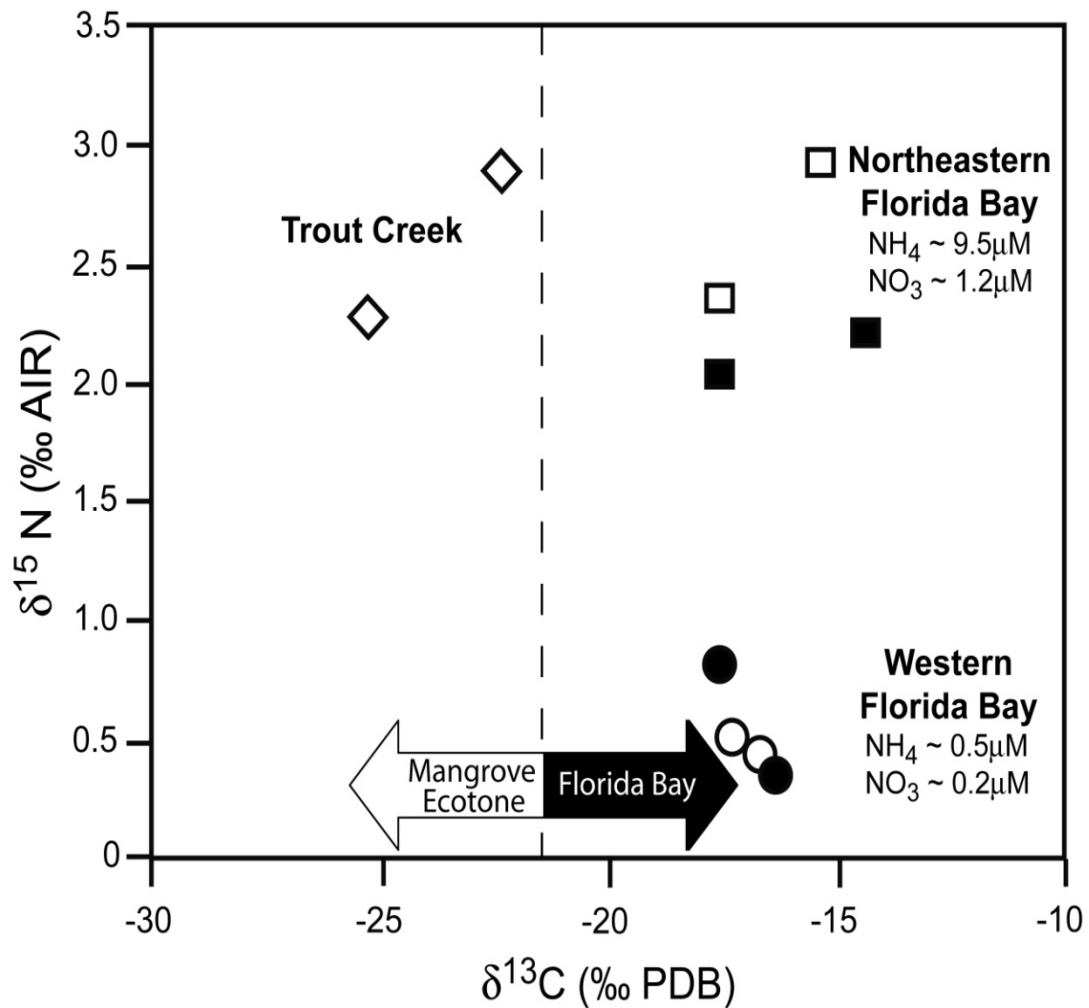


Figure 2.4 Stable isotope signals in 0.1-50mm POM collected in November 2003. Everglades outflow: Trout Creek (\diamond); Northeast Florida Bay: South Nest Key (\square), Duck Key (\blacksquare); Western Florida Bay: Ninemile Bank (\circ), and Sprigger Bank (\bullet).

al. 2004, Frankovich et al. 2006). Indeed, the physical and chemical variability of the system and the isolated nature of the various basins of Florida Bay certainly lead to the high level heterogeneity in planktonic communities. Populations of *Synechococcus* sp. were present throughout the bay (Figure 2.2; Cyanobacteria 3), however in higher abundances in northeastern Florida Bay than in the west. In fact, the highest abundance of *Synechococcus* sp. was found at Trout Creek, the lowest salinity site, proximal to Everglades' freshwater outflow. The dominance of this species in the northeastern,

strongly P-limited region of Florida Bay (Fourqurean et al. 1993) supports the conclusions of Stockner (1988) that *Synechococcus* sp. is a superior competitor for phosphorus, coupling high SRP affinity with rapid uptake velocities and the facility for luxury uptake. In addition, this genus is very well adapted to changing environmental conditions, exhibiting a broad range of salinity tolerance, the ability to saturate photosynthesis and growth at very low irradiance, and potential to assimilate dissolved organic nutrients (Stockner, 1988, Philips et al. 1989, Luo & Mitsui 1994, Lavrentyev et al. 1998, Glibert et al. 2004). In contrast, Cyanobacteria 4, with higher chlorophyll, and slightly larger-sized cells, were absent from Trout Creek and present in lower abundance in the northeastern bay as compared to the western stations. This may indicate that Cyanobacteria 4 are less tolerant of low salinities and less competitive in nutrient acquisition than typical Florida Bay *Synechococcus* sp.

The most abundant population found throughout Florida Bay in this study was *Synechococcus elongatus*, a larger, phycocyanin-rich strain of the genus exhibiting lower phycoerythrin than the population previously discussed (Philips et al. 1999). The *S. elongates* population represented 80 and 84% of the phytoplankton numerical abundance in western Florida Bay at Sprigger and Ninemile Banks, respectively. These proportions are somewhat lower than those observed by Glibert et al. (2004) during an extensive bloom in November 2002 where *S. elongatus* represented over 99% of the phytoplankton abundance in western and north-central Florida Bay. Further, *S. elongatus* represented over 90% of phytoplankton biovolume during fall blooms between 1993 and 1997, though no directly comparable numerical abundance values were given (Philips et al. 1999). There are several possible explanations for apparent differences between the

relative proportions of *S. elongatus* measured in this and prior studies, the most obvious being a smaller bloom in 2003 relative to previous years. Also, values reported here may represent either the early or late period in terms of bloom development, and might not correspond to peak bloom abundance. Furthermore, the maximum abundances noted by both Phlips et al. (1999) and Glibert et al. (2004) were located at sites in the north central region of Florida Bay, rather than the western boundary zone described here; thus it is possible that the high abundances of *S. elongatus* found in western Florida Bay in the present study were coincident with much greater populations that were not sampled at more interior locations. Long term chlorophyll A datasets indicate peak concentrations in Whipray Basin, North-central Florida Bay, exceeded those in the western region and were reached in October 2003. Concentrations in both regions had begun to decline in November (SERC-FIU Water Quality Monitoring Network).

The dominance of *S. elongatus* at the western Florida Bay endmember has interesting implications in terms of both nutrient availability and stable isotopic signatures. Depleted $\delta^{15}\text{N}$ isotopic signatures in the western bay during the *S. elongatus* bloom in November 2003 differed markedly from nitrogen isotopic values of 4.2‰ recorded during a similar bloom in November 2002 (Glibert et al. 2004). Isotopic depletion during a cyanobacterial bloom opposes the expectation that high primary productivity and surface nutrient utilization induces isotopic enrichment, as has been reported in many studies of oceanic and lacustrine POM (Ostrom et al. 1997; Altabet et al. 1999, Teranes & Bernasconi 2000, Schubert & Calvert 2001). Here, the 0.1-50 μm POM had $\delta^{15}\text{N}$ values characteristic of nitrogen fixing bacteria/cyanobacteria, which are habitually near 0‰ in terms of $\delta^{15}\text{N}$, reflecting the isotopic signature of atmospheric

nitrogen (Gu & Alexander 1993, Liu et al. 1996, Mahaffey et al. 2003). The ^{15}N -depletion may suggest that nitrogen fixation represents a significant nutrient source for this population, which is consistent with several studies of potential aerobic N-fixation in *Synechococcus* species, including *S. elongatus* (Duerr, 1981, Philips et al. 1989, Luo & Matsui 1994, Philips & Badylak 1996, Church, 2005). Although nitrogenase activity had been documented in *Synechococcus* sp. cultures in the past (i.e. Duerr, 1981), until recently, unicellular cyanobacteria were not considered important contributors to oceanic nitrogen fixation. However, recent molecular-based techniques identifying nitrogenase gene expression have suggested an active role in nitrogen fixation for these groups (Falcón et al. 2004, Church 2005). DIN concentrations approximately an order of magnitude lower than in the eastern bay and low DIN:SRP ratios in western Florida Bay, indicative of N-limitation of phytoplankton growth, might provide competitive advantage to nitrogen fixing cyanobacteria in this region. Similar results have been documented in benthic microalgae. Nagel (2004) measured nitrogen fixation along a west-east transect of Florida Bay at the sediment-water interface, finding orders of magnitude higher N-fixation in the N-limited western end of the transect in comparison to eastern sites.

Other components of the 0.1-50 μm POM that may contribute to the differences in the nitrogen isotopic signal between Florida Bay regions are the heterotrophic bacteria and particulate detritus concentrations observed. Western Florida Bay exhibited much higher abundances in both these particulate categories. While specific populations of the bacterial component were not identified, two clusters displaying high red fluorescence were abundant in the western bay, but were only present at very low abundances at the northeastern open marine sites. It would seem that the very high detritus and bacterial

abundance in western Florida Bay are related to the *S. elongatus* bloom; however, since samples amalgamating all components of the 0.1-50 μ m POM were analyzed for their isotopic signature, it is impossible to separate the relative importance of each component in terms of $\delta^{15}\text{N}$ value differences between regions. Yet, it is generally accepted that microbial degradation of autochthonous particulate organic material in marine systems tends to enrich the residual POM by remineralizing isotopically depleted NH_4^+ (Liu et al. 1996); however, the overall POM signal presented here is depleted in the region corresponding to the higher bacterial and detrital abundances.

The northeastern Florida Bay 0.1-50 μ m POM fraction exhibited nitrogen isotope signatures more characteristic of nutrient recycling in estuarine waters. However, at +2.0‰ to +3.0‰, these signatures are depleted relative to values in reported many estuaries (and very depleted relative to values measured in highly eutrophic settings; Middleburg & Nieuwenhuize 2001), which can vary widely, depending on trophic status and anthropogenic nitrogen impacts. Estuarine POM $\delta^{15}\text{N}$ values range from +4‰ to >+20‰, although few, if any, of these estuaries represent the oligotrophic regime characteristic of Florida Bay (Montoya et al. 1991, Rolff & Elmgren 2000, Middleburg & Nieuwenhuize 2001). Nitrogen isotopic values from oligotrophic open-ocean settings tend to reflect the isotopic signals of upwelled nitrate (\approx +5.0‰) altered in some cases by enrichment due to nutrient utilization or denitrification (Miyake & Wada 1967, Liu & Kaplan 1989; Schubert & Calvert 2001). In northeastern Florida Bay, isotopically light POM may reflect the assimilation of nitrogen discharged through the Everglades outflow. Uptake of a relatively depleted nitrogen source delivered by Everglades freshwater outflow is supported by the similarity between the low salinity mangrove ecotone Trout

Creek signal and the two northeast bay open water sites. Similar to differences noted at the western stations, the depleted POM signal in northeast Florida Bay is much more depleted than nitrogen isotopic values measured by Glibert et al. (2004) in Little Madeira Bay, November 2004 (+8.63‰). Little Madeira Bay is located within 5 km of all northeastern locations sampled in the work presented here. The differences between these studies (November 2002 versus November 2003) reflect the variable nature of the system in terms of water quality, nutrient sources, and storm induced perturbations. The potential that the comparatively depleted estuarine isotopic signal reported here indicates uptake of an isotopically light nitrogen source may be supported by the fact that ammonium concentrations were nearly tenfold higher than nitrate concentrations at the northeastern sites in November 2003. The $\delta^{15}\text{N}$ signatures of phytoplankton incorporating remineralized ammonium are more depleted (Checkley & Entzeroth 1985), and ^{15}N -tracer experiments confirmed that NH_4^+ is generally assimilated preferentially over NO_3^- in most phytoplankton (Montoya et al. 1991, Maguer et al. 2000, Velinsky & Fogel 1999). High NH_4^+ concentrations in northeastern Florida Bay suggest NH_4^+ as the predominant nitrogen source for primary production, causing observed $\delta^{15}\text{N}$ signatures in this region. Nitrification of an isotopically light ammonium source might also produce an isotopically depleted nitrate pool, which could be assimilated by phytoplankton (Cifuentes et al. 1989). Because inorganic phosphorus concentrations are persistently limiting in this region, it is unlikely that primary productivity increases generate high enough nitrogen uptake rates to deplete available pools, and thus no isotopic enrichment of photosynthetic autotrophs is evident.

Carbon isotopic signatures did not differ between northeastern and western Florida Bay, suggesting similar carbon acquisition mechanisms and/or relative carbon limitation between plankton communities in different regions of the bay. The $\delta^{13}\text{C}$ values of -17.6‰ to -14.4‰ fell within the published range of values from estuarine phytoplankton (Gearing et al. 1984, Velinsky & Foge 1999, Rau et al. 2001). Although the more enriched values may indicate some degree of carbon limitation or a shift toward a carbon concentration mechanism (CCM) whereby bicarbonate (HCO_3^-) is used as a carbon source. HCO_3^- becomes the dominant dissolved inorganic carbon (DIC) species available under conditions of increasing pH related to high photosynthetic uptake of dissolved CO_2 . A number of studies have demonstrated that many microalgal genera, including *Synechococcus*, are capable of switching to a CCM that facilitates assimilation of HCO_3^- in response to increasing HCO_3^- concentrations and dissolved CO_2 limitation. (Badger & Andrews 1982, Mayo et al. 1986, Fogel et al. 1992, Popp et al. 1998, Matsuda et al. 2001, Rau et al. 2001). It is reasonable then, that the cyanobacterial populations at both northeastern and western Florida Bay stations employ this mechanism under carbon stress. Yet, high photosynthetic rates assumed inherent in cyanobacterial blooms are not reflected by POM $\delta^{13}\text{C}$ enrichment under carbon limitation and decreases in isotopic discrimination. Open connectivity between western Florida Bay and the Gulf of Mexico, and diurnal tidal exchange may serve to maintain DIC availability at a similar level to that in northeastern Florida Bay even though the northeast exhibits much lower productivity levels. An alternative explanation for the relatively enriched $\delta^{13}\text{C}$ values of marine Florida Bay stations is the fact that seagrass detritus may represent either a significant component of the particulate detritus, or may represent a carbon source used

by the microbial community. Seagrass $\delta^{13}\text{C}$ signatures are more enriched than those typical for C_3 plants, varying seasonally between -13.5‰ and -5.2‰, likely attributable to an active CCM and HCO_3^- uptake (Fourqurean et al. 2005, Anderson & Fourqurean 2003). Seagrass associated carbon, either in the form of microbially released dissolved CO_2 or as a particulate detritus component of the 0.1- 50 μm POM, would serve to generate the more enriched carbon isotopic values evident at marine stations in Florida Bay.

The $\delta^{13}\text{C}$ signature of the Trout Creek 0.1-50 μm POM fraction was more isotopically depleted than those at open water marine sites. This ^{13}C depletion may reflect different carbon sources between the brackish mangrove ecotone and open marine systems, perhaps indicating that the Trout Creek outflow is influenced by dissolved or particulate organic carbon associated with terrestrial sources (Kendall & McDonnell 1998). This contention is supported not only by the station's proximity to the mangrove ecotone of the southern Everglades, but also by a more than fourfold higher concentration of detritus at the Trout Creek site, compared to the open marine sites in northeastern Florida Bay. The carbon isotopic signatures evident at the station imply that a large component of the detritus is likely of mangrove origin with some autochthonous inputs from the water column community.

2.6 CONCLUSION

The isotopic composition of POM in near-shore and estuarine settings can provide important information about ambient environmental conditions, biotic community

structure, and biogeochemical cycling within the system. This information may be used to infer changes in primary productivity and water quality parameters in increasingly environmentally sensitive coastal settings. Combining flow cytometry with stable isotopic analyses provides unique insight into ecological controls on carbon and nitrogen isotopic signatures of POM, improving interpretations. In many marine settings, carbon and nitrogen isotopic signatures have been interpreted in terms of surface nutrient utilization and productivity levels, yet here we present data from a cyanobacterial bloom showing nitrogen isotopic depletion, rather than enrichment. This isotopic depletion has implications regarding the importance of biologically fixed nitrogen as a nutrient source during bloom events, particularly in nitrogen-limited marine environments. Further work examining other indicators of N-fixation, such as nitrogenase enzymatic assays or mesocosm experimentation measuring uptake of isotopically labeled N_2 gas, is needed to elucidate the role fixed nitrogen plays in South Florida coastal environments.

The spatial variability evident in Florida Bay planktonic species assemblages, detritus concentrations, and corresponding isotopic compositions suggests that bulk POM isotopic values combining all size fractions may not be easily attributed to external nutrient forcings without closer examination. More extensive size-fractionated POM sampling, distributed geographically and over longer term time-series development, is necessary to more fully understand carbon and nitrogen cycling within the South Florida coastal zone. Further work examining temporal variability in planktonic assemblages and corresponding isotopic compositions, taken in conjunction with water quality variables and the isotopic composition of dissolved inorganic nutrient compounds will greatly

enhance understanding of nitrogen and carbon cycling in Florida Bay and adjacent marine systems.

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CHAPTER 3

SPATIAL AND TEMPORAL VARIABILITY IN THE ISOTOPIC COMPOSITION OF PARTICULATE ORGANIC MATERIAL: SOURCES, CONTROLS, AND EPISODIC CHANGE

3.1 ABSTRACT

Understanding the variability in carbon and nitrogen isotopic composition of particulate organic material (POM) in the coastal zone is crucial to studies of biogeochemical processes in marine environments. This is particularly true in South Florida as long term plans for restoration of natural flow conditions through the Everglades increase the importance of understanding baseline characteristics of the system in terms of nutrient cycling and biogeochemistry. Additionally, while many studies apply bulk POM isotopic and elemental compositional data to ecological problems, there is little consideration given to the components integrated in bulk particulate signatures. In this study, isotopic compositions ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) of three size fractions of particulate organic matter (0.1-50 μm , 50-150 μm , and >150 μm) from ten locations in Florida Bay and the Florida Keys National Marine Sanctuary were determined on a quarterly basis over a 2-year period in order to examine seasonality and spatial variability in isotopic values of POM size components. Significant differences were observed among both size classes and locations in terms of isotopic values and seasonal patterns. $\delta^{13}\text{C}$ values varied between -29.59 and -7.4‰ while $\delta^{15}\text{N}$ values ranged from +1.44 to +8.52‰. Isotopic enrichment-depletion cycles varied on a quarterly basis; however, patterns differed among locations related to local hydrodynamic influences. Larger amplitude changes were found in Florida Bay sampling locations as compared to sites along the Florida Keys Reef Tract.

3.2 INTRODUCTION

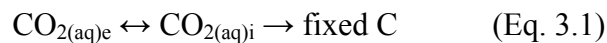
The combined measurement of carbon and nitrogen natural abundance isotopic ratios, expressed as $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, of suspended particulate organic matter (POM) have proven useful in aquatic biogeochemistry and ecology to assess the origin (terrestrial, freshwater, or marine reservoir) and fate of POM (Gearing 1988, Altabet 1988, Matson and Brinson 1990, Thornton and McManus 1994, Cifuentes et al. 1996, Sigleo and Macko 2002). Carbon and nitrogen isotopic values have also been applied in efforts to gauge surface nutrient utilization by autotrophs and clarify metabolic pathways (Goericke et al. 1994, Altabet 2001, Savoye et al. 2003), to study C and N cycles (Altabet et al. 1999, Battle et al. 2000) and to describe food web trophic relationships (Fry and Sherr 1984, Peterson 1999). Most of these studies, however, focused either on bulk organic material (undifferentiated plankton tow collection, bulk filtrations, total surface sediments, etc.), or on higher level invertebrate or vertebrate consumers (Rau et al. 1990). There have been relatively few studies characterizing $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in discrete size classes of POM with the intent to differentiate between isotopic signals associated with various taxonomic and trophic groups integrated in bulk measurements. Given the variability in production mechanisms/nutrient acquisition, as well as trophic and feeding differences occurring across plankton size classes (Rau et al. 1990, Wainright and Fry 1994, Rolff 2000, Sato et al. 2006, Loick et al. 2007), there is considerable potential for isotopic heterogeneity between size fractional isolates of bulk POM. Further, considering rapid turnover rates and the tight association between planktonic communities and water quality, POM can potentially impact ecological function and biogeochemical properties

of the coastal zone. Thus, better understanding of processes and interactions between particulate components is essential to more complete understanding of the shallow coastal interface between terrestrial and marine systems.

Estuarine POM is composed of several components of different origins, including in situ autochthonous plankton, higher plant detritus transported by rivers or sloughs, and local submerged aquatic vegetation and re-suspended organic sediment. Stable carbon isotopic composition has been conventionally used to discriminate between autochthonous marine (comparatively enriched $\delta^{13}\text{C}$) and allochthonous terrestrial (more depleted $\delta^{13}\text{C}$) organic carbon sources (Coffin et al. 1994). Nitrogen isotopic composition also often shows clear difference between terrestrial and marine origins (Peters et al. 1978, Mariotti et al. 1984, McClelland and Valiela 1998, Umezawa et al. 2002), and has been used to evaluate terrestrial nitrogen input to estuaries in combination with $\delta^{13}\text{C}$ (e.g. Wada et al. 1987, Thornton and McManus 1994, Middleburg and Nieuwenhuize 1998). However, interpretation of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ signatures is not without caveat when the isotopic values of terrestrial or marine end members are inconsistent over time (Gearing et al. 1984, Ogawa et al. 1994), particularly in estuarine settings where nutrient fluxes from adjacent terrestrial systems are variable and seasonal blooms of phytoplankton are common. Furthermore, phytoplankton isotopic values vary widely throughout aquatic ecosystems (Gearing 1988, Rau et al. 1990, Wada and Hattori 1991, Wainright and Fry 1994, Rolff 2000, Savoye et al. 2003, Sato et al. 2006 and others) due to numerous factors. The main controls over phytoplankton isotope signature can be summarized as: (1) The isotope ratio of the nutrient source (Owens 1987, Fry 1996); (2) the isotope effects associated with nutrient assimilation (Park and Epstein 1960, O' Leary

1981, Fogel and Cifuentes 1993, Montoya and McCarthy 1995, Pennock et al. 1996, Waser et al. 1998, 1999, Needoba et al. 2003, 2004) and (3) the isotope effects associated with biosynthesis (Descolas-Gros and Fontugne 1990, Wada and Hattori 1991, Bentaleb et al. 1998, Riebesell 2000). In particular, nutrient availability and isotopic fractionation during nutrient incorporation are of major importance (Rau et al. 1992, Pennock et al. 1996, Korb et al. 1998, Altabet 2001). In terms of nitrogen, because the lighter isotope is preferentially incorporated over the heavier one, nutrient uptake results in enrichment of the heavier isotope in the residual nutrient pool. When the ambient nutrient stock is at high concentration and/or when nutrient demand is low, this enrichment becomes negligible; when the nutrient stock declines (during the course of a plankton bloom), ^{15}N -enrichment increases and the isotope ratio of the phytoplankton incorporating residual nutrient rises. This represents the classic isotopic example of Rayleigh fractionation during surface nutrient utilization which has been invoked in open-ocean systems (Wada 1980, Altabet and Francois 1994, Altabet et al. 1999), coastal ecosystems (Goering et al. 1990, Horrigan et al. 1990), and lake settings (Teranes and Bernasconi 2000).

In terms of $\delta^{13}\text{C}$, the inverse relationship between fractionation and the growth rate/ $[\text{CO}_2]_{\text{aq}}$ ratio has been well documented (Laws et al. 1995, 1997, Popp et al. 1998, Burkhardt et al. 1999). The influence of phytoplankton growth rate on isotopic fractionation is more specifically defined by the 2-step model of carbon fixation described by Fry (1996):



where $\text{CO}_{2(\text{aq})\text{e}}$ and $\text{CO}_{2(\text{aq})\text{i}}$ are cell-external and –internal dissolved inorganic carbon pools, respectively. The first step (reversible) consists of the $\text{CO}_{2(\text{aq})}$

incorporation/transport (with the possibility of re-release of $\text{CO}_{2(\text{aq})}$ from the internal pool back to the external pool) associated with very low fractionation. The second step (irreversible) is the enzyme catalyzed carboxylation (photosynthetic fixation) associated with potentially large fractionation (Farquhar et al. 1982, Fry 1996). If the photosynthesis rate is low (ie. low growth rate, low nutrient demand), the intracellular CO_2 pool is large and uptake rate is limited by the carboxylation reactions. Because of the large fractionation during carboxylation, fractionation for the complete reaction is thus high. In contrast, at high photosynthesis rates (i.e. high growth rate, high nutrient demand), the intracellular carbon pool diminishes as it is rapidly utilized and assimilation rate is limited by the membrane transport of the first step. If all the carbon entering the cell is utilized, little or no fractionation occurs during the whole reaction (Farquhar et al. 1982, Bentaleb et al. 1998).

The final fractionation product of either nitrogen or carbon assimilation is dependent on initial nutrient source isotopic composition, consequently the isotopic signatures of the autochthonous particulate organic carbon and nitrogen may fluctuate, reflecting temporal changes in nutrient sources and metabolic activities (Cifuentes et al. 1988, Ogawa and Ogura 1997, Hellings et al. 1999, Rudnick et al. 1999). Nutrient fluxes from both oceanic and terrestrial Everglades nutrient sources vary extensively on a seasonal basis in the South Florida coastal system. Upwelling events episodically supply the Florida reef tract with influxes of new nutrients (Leichter et al. 2003), while other storm events and weather-driven surface currents transport nutrient fluxes across the western Florida Bay boundary with the Gulf of Mexico and across the Middle Florida Keys channels (Smith 1998, Gibson et al. 2008). Management of freshwater resources in

the Everglades generates variable nutrient inputs due to water storage in the water conservation areas, punctuated with pulse releases that may or may not mimic seasonal rainfall patterns. Residence time within the storage areas may significantly influence the nutrient species and isotopic composition of the dissolved nutrients later delivered to the downstream coastal zone. Thus a variety of cycling processes and differentiated nutrient sources may be intermingled in the coastal system, complicating the understanding of nutrient cycling and the interpretation of the isotopic composition of autochthonous organic material produced through utilization of variable nutrient resources.

In light of current restoration efforts ongoing in the Everglades drainage system and long term plans to increase freshwater flows to downstream Florida Bay, understanding current variability in the system will become key to understanding the changes sure to develop as restoration progresses. Recent work by Xu and Jaffé (2007) demonstrated significant spatial and temporal variability in Florida Bay POM composition based on a suite of organic biomarker analyses. They concluded that autochthonous marine OM sources were the principle contributors to Florida Bay POM, particularly during the wet season. Spatially, there was a shift in OM sources from marine plankton/seagrass in the SW to mangrove-derived terrestrial material in the NE bay adjacent to the mangrove ecotone; this shift was most evident in the dry season when planktonic productivity declined (Xu and Jaffé 2007). The present study builds upon previous work in order to better understand the sources of seasonal and spatial fluctuation in POM from an isotopic perspective. Size fractionated POM samples were collected on a quarterly basis between September 2002 and January 2005. The purpose of this work was to examine seasonal and spatial isotopic dynamics in different size fractions of POM

in an effort to separate zooplankton and detrital components, phytoplankton, and cyanobacteria and bacteria into broad groups. Planktonic groups can be expected to respond quickly to changes in water quality, and variations in their geochemical composition may be attributed to environmental parameters. Distinct isotopic fingerprints based on speciation, degree of nutrient utilization, switches between varying N and C sources, and N vs C limitation may all play a part in influencing the isotopic signatures of different size fractions.

3.3 METHODS

3.3.1 Sampling Protocol

Sampling of particulate organic matter was conducted on a quarterly basis beginning Sept. 2002 and continuing through Jan. 2005 at 10 sites located within the Florida Keys National Marine Sanctuary and Florida Bay (Figure 3.1; Table 3.1). Samples were collected using a portable pump system (2000 gph bilge pump fitted with a 1.5 inch diameter flexible hose; 12 V deep cycle marine battery) and two stacked Nitex mesh sieves (150 μ m, 50 μ m) made from 6-inch PVC and marine hose clamps. The upper 1.5 m of water column was sampled for 30 minutes, allowing more than 3500L of water to pass through the sieve system. The >150 μ m and 50-150 μ m samples were rinsed with deionized water from Nitex screens into 30 ml bottles immediately following the sampling interval and were kept on ice for transport to the laboratory. These two size fractions were broadly characterized in terms of speciation using traditional light microscopy. A water sample (1L) was collected after passing through the sieves (the 0.1-

50µm size fraction), which was kept on ice until filtration on Whatman Anodisc

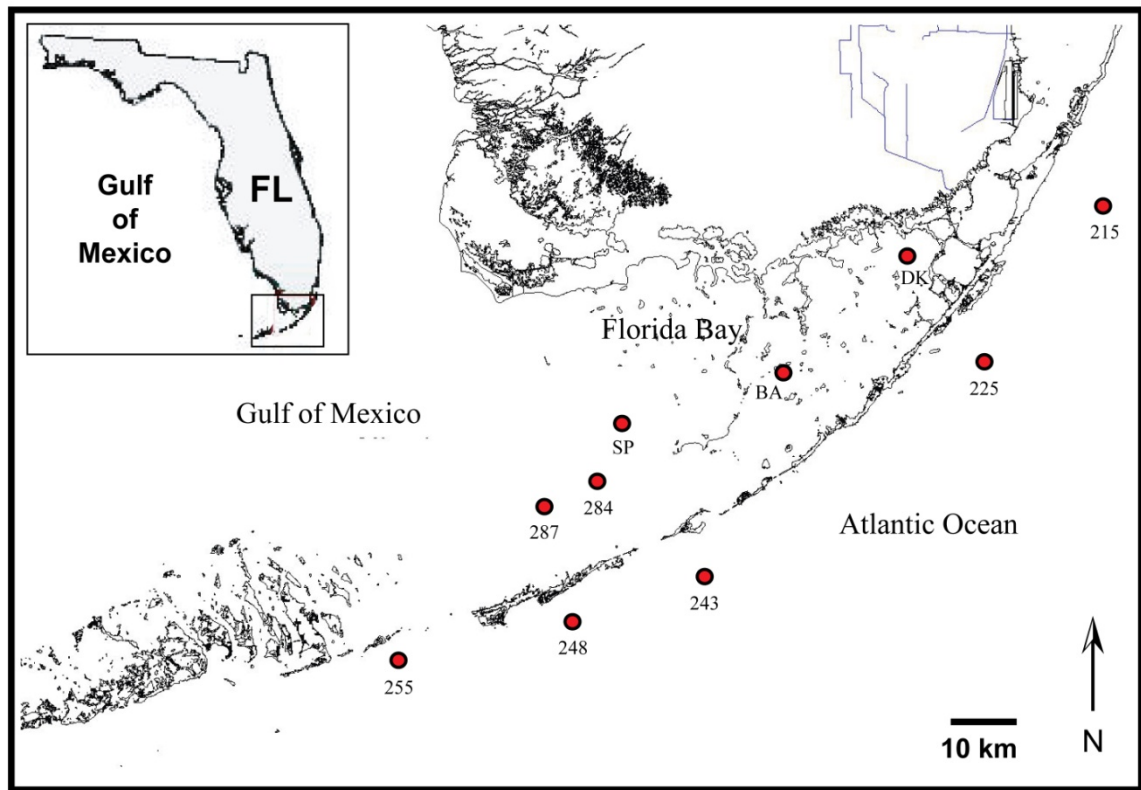


Figure 3.1 Map of Florida Bay and the Florida Keys National Marine Sanctuary, showing POM sampling sites on the Atlantic Ocean side of the Florida Keys: Carysfort Reef (215), Molasses Reef (225), Tennessee Reef (243), Coffins Patch Channel (248), Bahia Honda Channel (255); and in Florida Bay: Tripod Bank (284), Bamboo Bank (287), Sprigger Bank (SP), Bob Allen Bank (BA), and Duck Key (DK).

Table 3.1 POM sampling site locations and mean depths

Site	Station number*	Latitude	Longitude	Mean Depth (m)
Carysfort Reef	215	25°13.314N	80°12.881W	6.1
Molasses Reef	225	25°00.807N	80°22.677W	3.4
Tennessee Reef	243	24°44.588N	80°47.799W	9.1
Coffins Patch Channel	248	24°41.155N	80°58.879W	9.1
Bahia Honda Channel	255	24°37.432N	81°14.725W	9.1
Tripod Bank	284	24°52.605N	80°57.507W	1.5
Bamboo Bank	287	24°50.800N	81°00.499W	2.1
Sprigger Bank	SP	24°54.771N	80°56.288W	0.75
Bob Allen Bank	BA	25°01.484N	80°40.859W	1.25
Duck Key	DK	25°10.617N	80°29.383W	1.7

* Identifier for SERC Water Quality Monitoring Network and FKNMS Seagrass Monitoring Project

membrane filters (0.1 μ m pore size) in the laboratory. Triplicate samples for FACS flow cytometer analyses of the 0.1-50 μ m size fraction (2ml) were also collected after passing through the sieves. Samples for FACS analyses were preserved with formalin to a 1% final concentration. Additional samples were collected from each site for bulk POM isotopic composition during the 2004 sampling quarters. For these samples 10L bulk seawater was collected and filtered at dockage on precombusted 0.45 μ m GF/C glass fiber filters. All size fractions and membrane filters were then dried at 70°C, powdered, and analyzed for stable isotope ratios following standard IRMS procedures as outlined previously (Evans et al. 2006).

3.3.2 Flow Cytometer Analyses

Flow Cytometer analyses of the 0.1-50 μ m POM fraction were completed for both heterotrophic bacteria and phytoplankton. Analyses of heterotrophic bacteria required a DNA staining procedure (Jochem 2000). For analyses of bulk phytoplankton samples, 1ml of each replicate sample was analyzed without further processing. All samples were analyzed on a Beckton Dickinson FACSort flow cytometer. SYBR DNA fluorescence was recorded in both the green (FL1) and red (FL3) fluorescence channels (heterotrophic bacteria), whereas the phytoplankton samples were assessed using chlorophyll autofluorescence, detected in the red (FL3) fluorescence channel. For proxy analysis of relative cell size, Side Angle Light Scatter is measured (SSC channel). All signals are recorded on a 4-decades log scale and all are analyzed using Win MDI 2.7 Software. DNA clusters of bacteria are counted by logical gating from both FL1 vs FL3 and SSC vs

FL1 dotplots and histograms with gate borders set to minima in population frequency distribution.

3.3.3 Statistical Analyses

Data were analyzed using a variety of parametric and non-parametric methods. One-Way Analysis of Variance was completed comparing 2-year datasets among sites and between size fractions within sites, followed by Holm-Sidak tests for post-hoc pairwise comparisons. Where problems with normality or equal variance occurred among data sets, the Kruskal-Wallis One-Way Analysis of Variance on Ranks was used in place of ANOVA and Dunn's test was used for post hoc pair-wise comparisons. Student's t-tests were used to compare paired, pooled data sets from Florida Bay versus Atlantic Ocean sites where variables were normally distributed, whereas the Mann Whitney Rank Sum Test was used where parametric tests were not appropriate. Pearson Product Moment Correlations were used to assess relationships among variables and water quality parameters, and simple regression analyses were also utilized. All statistical analyses were completed using SigmaPlot 8.0, Systat Software, 2004.

3.4 RESULTS

3.4.1 Time Series

A high level of spatial and temporal variability is evident in time-series plots of the 2-year size fractionated isotopic dataset from 10 sites in the Florida Keys National Marine Sanctuary (Atlantic Ocean side of the Florida Keys) and within Florida Bay

(Figures 3.2-7). Mean isotopic compositions, as well as minima and maxima for each size fraction at all stations are summarized in Table 3.2. Figure 3.2 combines data sets from the two northernmost locations sampled, adjacent to two reefs off the Atlantic coast of Key Largo, Carysfort Reef and Molasses Reef. Nutrient concentration data for nitrate (NO_3^-), ammonium (NH_4^+), and soluble reactive phosphorus (SRP) are courtesy of the

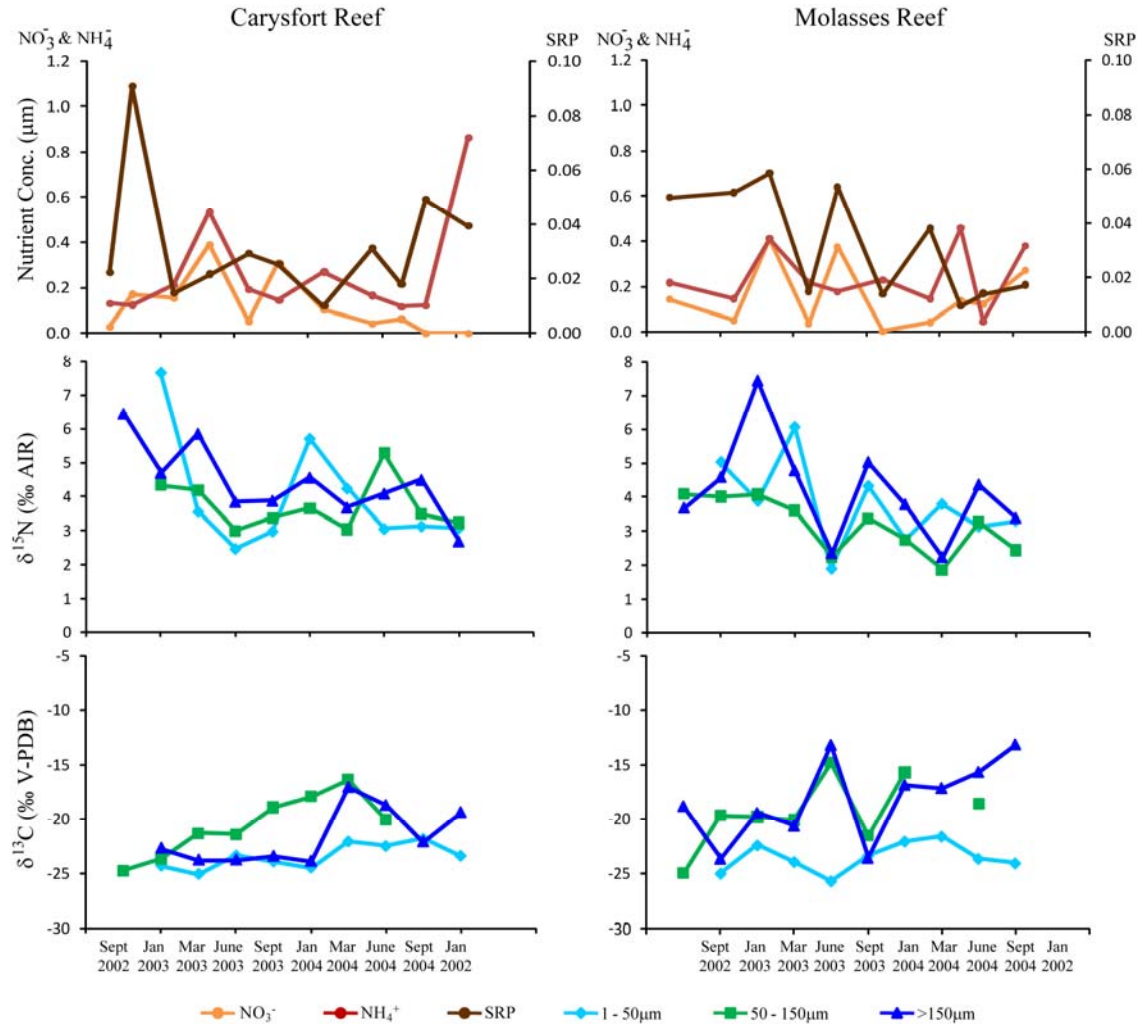


Figure 3.2 Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from reef settings in the northern Florida Keys. Nutrient concentration data (nitrate, ammonium, and soluble reactive phosphorus) are also shown.

Table 3.2 Descriptive statistics for each POM size fraction collected from 10 sites in Florida Bay and the Florida Keys National Marine Sanctuary.

Site	Size Fraction	$\delta^{15}\text{N}$ (‰ AIR)						$\delta^{13}\text{C}$ (‰PDB)						Molar C:N					
		Mean \pm St. D.		Range	Max	Min	Mean \pm St. D.		Range	Max	Min	Mean \pm St. D.		Range	Max	Min			
Carysfort Reef	0.1-50 μm	3.99	\pm 1.68	5.20	7.68	2.48	-23.41	\pm 1.12	3.25	-21.81	-25.06	12.77	\pm 4.56	32.21	37.21	5.13			
	50-150 μm	3.75	\pm 0.74	2.27	5.29	3.02	-20.53	\pm 2.80	8.33	-16.37	-24.70	12.17	\pm 5.49	13.89	18.39	4.50			
	>150 μm	4.43	\pm 1.08	3.75	6.45	2.70	-21.65	\pm 2.57	5.70	-17.07	-23.77	9.01	\pm 9.20	27.03	27.87	0.84			
Molasses Reef	0.1-50 μm	3.80	\pm 1.24	4.16	6.06	1.90	-23.52	\pm 1.35	4.12	-21.58	-25.70	6.63	\pm 1.78	5.71	8.44	2.73			
	50-150 μm	3.17	\pm 0.80	2.19	4.07	1.89	-19.33	\pm 3.46	10.18	-14.78	-24.96	19.07	\pm 8.34	22.83	30.74	7.90			
	>150 μm	4.16	\pm 1.49	5.21	7.44	2.23	-18.21	\pm 3.76	10.55	-13.12	-23.67	9.36	\pm 7.20	19.90	21.01	1.11			
Tennessee Reef	0.1-50 μm	3.16	\pm 1.30	4.42	6.41	1.98	-23.39	\pm 1.14	3.87	-21.64	-25.51	13.81	\pm 13.55	41.31	45.81	4.50			
	50-150 μm	3.63	\pm 0.91	2.98	5.56	2.58	-20.50	\pm 2.53	7.69	-16.91	-24.60	9.38	\pm 9.36	27.07	28.65	1.58			
	>150 μm	4.16	\pm 1.34	5.21	6.55	1.35	-20.90	\pm 2.29	7.32	-16.74	-24.06	8.49	\pm 4.01	14.47	17.11	2.64			
Coffins Patch Channel	0.1-50 μm	2.32	\pm 0.77	2.31	3.77	1.46	-22.79	\pm 1.09	3.48	-20.58	-24.06	7.83	\pm 4.04	14.57	17.46	2.89			
	50-150 μm	3.49	\pm 0.68	2.51	4.80	2.29	-18.34	\pm 3.17	11.24	-13.10	-24.34	9.62	\pm 7.45	24.41	26.82	2.41			
	>150 μm	4.38	\pm 0.46	1.47	5.07	3.60	-18.91	\pm 3.10	9.33	-14.37	-23.70	10.31	\pm 3.91	11.57	17.23	5.65			
Bahia Honda Channel	0.1-50 μm	2.36	\pm 0.77	2.13	3.57	1.44	-22.05	\pm 1.76	5.23	-19.33	-24.56	6.55	\pm 4.44	13.69	17.29	3.60			
	50-150 μm	3.82	\pm 0.55	1.85	5.03	3.18	-19.25	\pm 2.73	9.29	-15.61	-24.90	8.08	\pm 7.97	24.63	27.57	2.95			
	>150 μm	4.45	\pm 0.99	3.05	5.72	2.67	-18.97	\pm 5.32	16.27	-10.53	-26.80	8.30	\pm 3.94	11.58	14.73	3.15			
Tripod Bank	0.1-50 μm	3.14	\pm 0.92	2.81	4.47	1.66	-21.14	\pm 1.81	5.53	-18.38	-23.91	6.18	\pm 2.33	5.80	9.40	3.61			
	50-150 μm	3.95	\pm 0.42	1.35	4.75	3.40	-16.45	\pm 2.36	5.58	-14.50	-20.07	7.58	\pm 3.32	9.31	13.37	4.06			
	>150 μm	3.90	\pm 1.77	6.40	8.39	1.99	-14.62	\pm 3.61	9.44	-10.62	-20.06	13.28	\pm 6.16	21.05	22.59	1.54			
Bamboo Bank	0.1-50 μm	2.13	\pm 0.57	1.85	2.94	1.09	-20.84	\pm 2.22	6.43	-17.81	-24.23	7.03	\pm 2.66	8.69	12.01	3.33			
	50-150 μm	3.72	\pm 0.43	1.60	4.38	2.78	-16.07	\pm 1.74	6.20	-13.76	-19.96	7.83	\pm 3.15	9.79	14.95	5.16			
	>150 μm	3.49	\pm 1.01	2.75	4.97	2.22	-15.64	\pm 4.05	13.25	-7.40	-20.65	9.03	\pm 5.82	14.77	17.02	2.25			
Sprigger Bank	0.1-50 μm	3.31	\pm 1.00	3.03	4.60	1.57	-24.04	\pm 3.76	11.34	-18.25	-29.59	17.05	\pm 25.62	70.49	73.28	2.79			
	50-150 μm	4.44	\pm 1.05	3.68	5.81	2.13	-17.61	\pm 3.74	12.67	-12.91	-25.58	10.31	\pm 5.70	19.81	23.50	3.68			
	>150 μm	3.76	\pm 0.97	3.12	5.09	1.97	-19.47	\pm 5.20	18.16	-10.79	-28.95	16.28	\pm 15.42	51.08	53.99	2.91			
Bob Allen Bank	0.1-50 μm	2.83	\pm 0.38	1.05	3.28	2.24	-15.43	\pm 3.65	10.67	-11.38	-22.06	5.84	\pm 3.85	9.39	12.32	2.93			
	50-150 μm	4.28	\pm 0.71	2.43	5.08	2.65	-15.24	\pm 1.95	5.72	-13.46	-19.18	16.75	\pm 5.06	14.37	24.51	10.15			
	>150 μm	4.37	\pm 0.67	1.82	5.58	3.76	-18.30	\pm 4.24	12.44	-12.98	-25.41	17.46	\pm 10.22	25.94	27.94	2.00			
Duck Key	0.1-50 μm	4.32	\pm 0.41	1.29	4.85	3.56	-20.06	\pm 4.65	13.77	-12.95	-26.72	10.99	\pm 4.60	13.74	19.17	5.42			
	50-150 μm	5.49	\pm 1.29	4.44	6.75	2.31	-18.17	\pm 1.61	4.75	-15.23	-19.97	19.27	\pm 8.27	24.37	34.30	9.93			
	>150 μm	6.06	\pm 1.51	4.61	8.52	3.91	-20.58	\pm 3.36	10.08	-16.17	-26.25	27.77	\pm 41.56	122.4	130.18	7.70			

Southeast Environmental Research Center Water Quality Monitoring Network (Florida International University)*¹ (Appendix 1).

Nitrogen isotopic compositions appear to be associated with nutrient availability at several intervals during the sampling period in all three POM size fractions at the reefs. Specifically, in the case of Carysfort Reef, enriched isotopic values in all three POM fractions seem to correspond to concentration increases in DIN (dissolved NO_3^- and NH_4^+), however this relationship is not consistently obvious over time. In the 0.1-50 μm and 50-150 μm fractions (the bacteria/cyanobacteria- and larger phytoplankton-associated size ranges) at both northern reef sites, January nitrogen isotopic values tended to be more enriched, while spring samplings showed more depleted signals. Although chlorophyll-*a* concentrations in the reef setting are habitually low, the winter samplings in 2003, 2004, and 2005 were coincident with intra-annual chlorophyll-*a* concentration maximums. Carbon isotopic values also exhibit high variability; however, a repetitive annual signal was only apparent in the 0.1-50 μm fraction at the Molasses Reef site, with repeated depletions in the winter sampling periods.

The Middle Florida Keys channel and patch reef time series are shown in Figures 3.3 and 3.4 (Tennessee Reef and Coffins Patch Channel, Figure 3.3; Bahia Honda Channel 3.4). These sites exhibit similar trends to the northern reef sites, demonstrating episodic relationships between pulsed nutrient inputs and changes in POM isotopic compositions. The 50-150 μm size fraction here too shows some evidence for annual cycling, with 2‰ nitrogen isotopic enrichments repeated in all March and June sampling

¹ Data were provided by the SERC-FIU Water Quality Monitoring Network which is supported by SFWMD/SERC Cooperative Agreement #4600000352 as well as EPA Agreement #X7-96410603-3

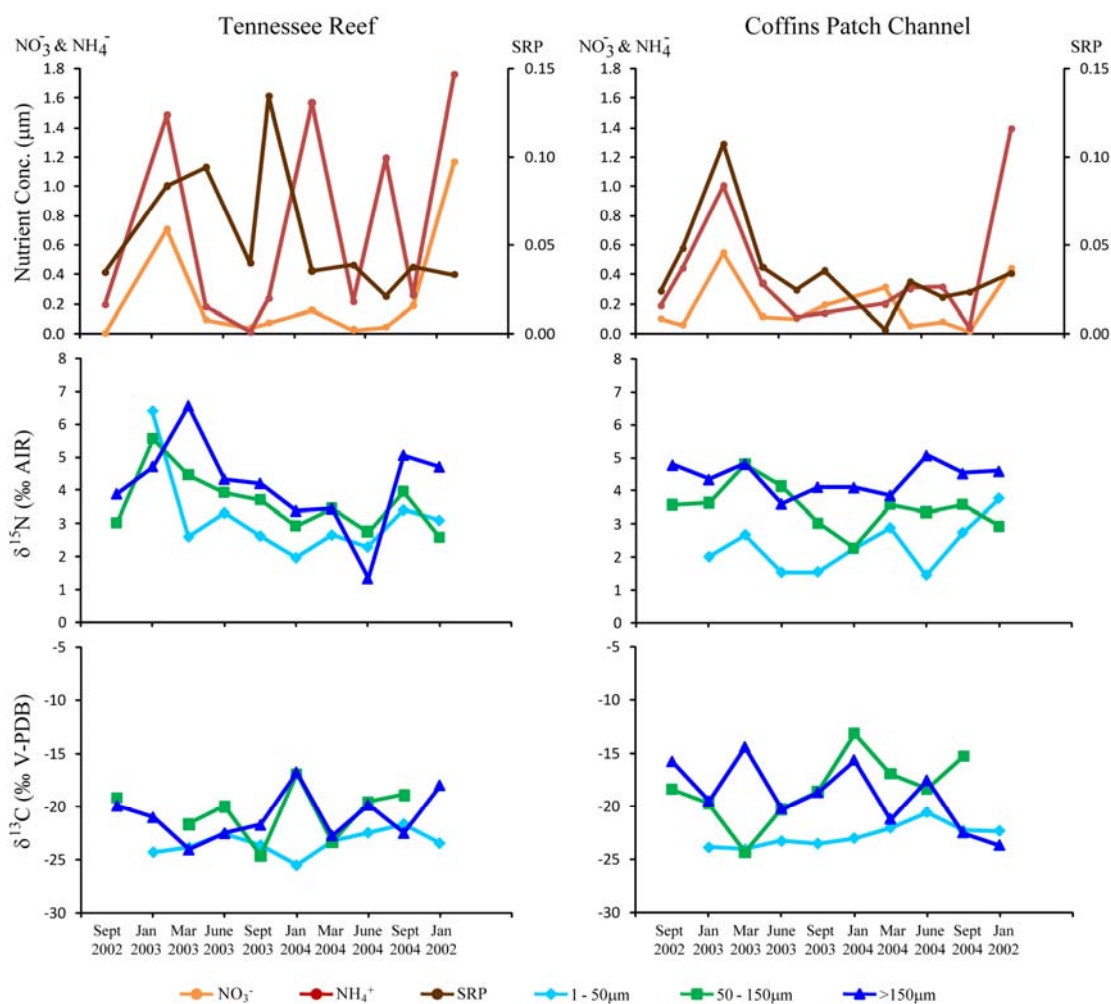


Figure 3.3 Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from reef and channel settings in the Middle Florida Keys. Nutrient concentration data (nitrate, ammonium, and soluble reactive phosphorus) are also shown.

events, while the January signal was repeatedly depleted. The same trend was apparent in the 0.1-50μm size fraction at the Middle Keys sites. $\delta^{13}\text{C}$ in particular showed depletions in successive January sampling events. Nitrogen isotopic changes in this size fraction were less clear, exhibiting January depletions at Tennessee Reef and Bahia Honda Channel, but the opposite trend at Coffins Patch Channel, which had enriched $\delta^{15}\text{N}$ values during winter sampling intervals and depleted signatures in the summer. Western Florida Bay sites, Tripod Bank, Bamboo Bank, and Sprigger Bank, are

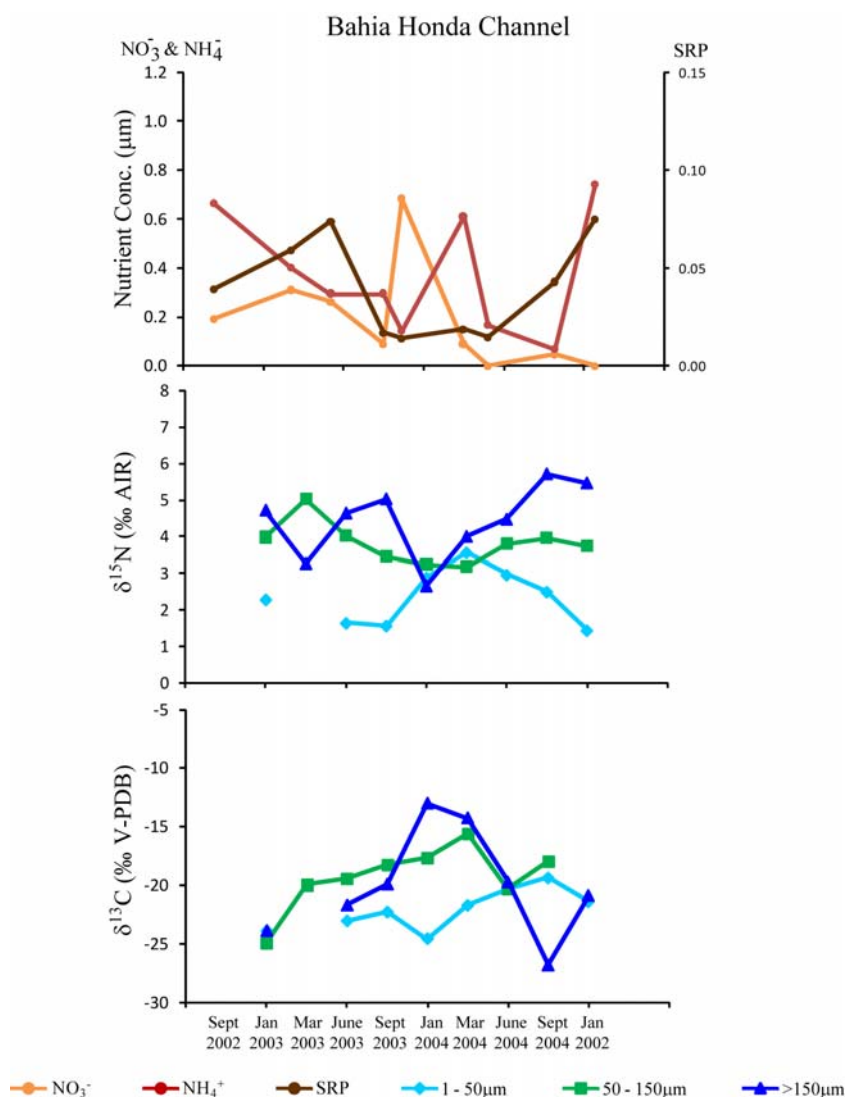


Figure 3.4 Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from a channel setting in the Middle Florida Keys. Nutrient concentration data (nitrate, ammonium, and soluble reactive phosphorus) are also shown.

shown in Figures 3.5 and 3.6. These sites were characterized by markedly low nutrient availability throughout the sampling period; however, as in the sites previously described, there was a relationship between the nutrient parameters and the POM isotopic values, with nitrogen isotopic enrichment and depletion cycles closely following nutrient availabilities. The most pronounced nitrogen isotope trends were evident in the 50-150µm and 0.1-50µm size classes at Tripod and Bamboo Banks, with more depleted $\delta^{15}\text{N}$

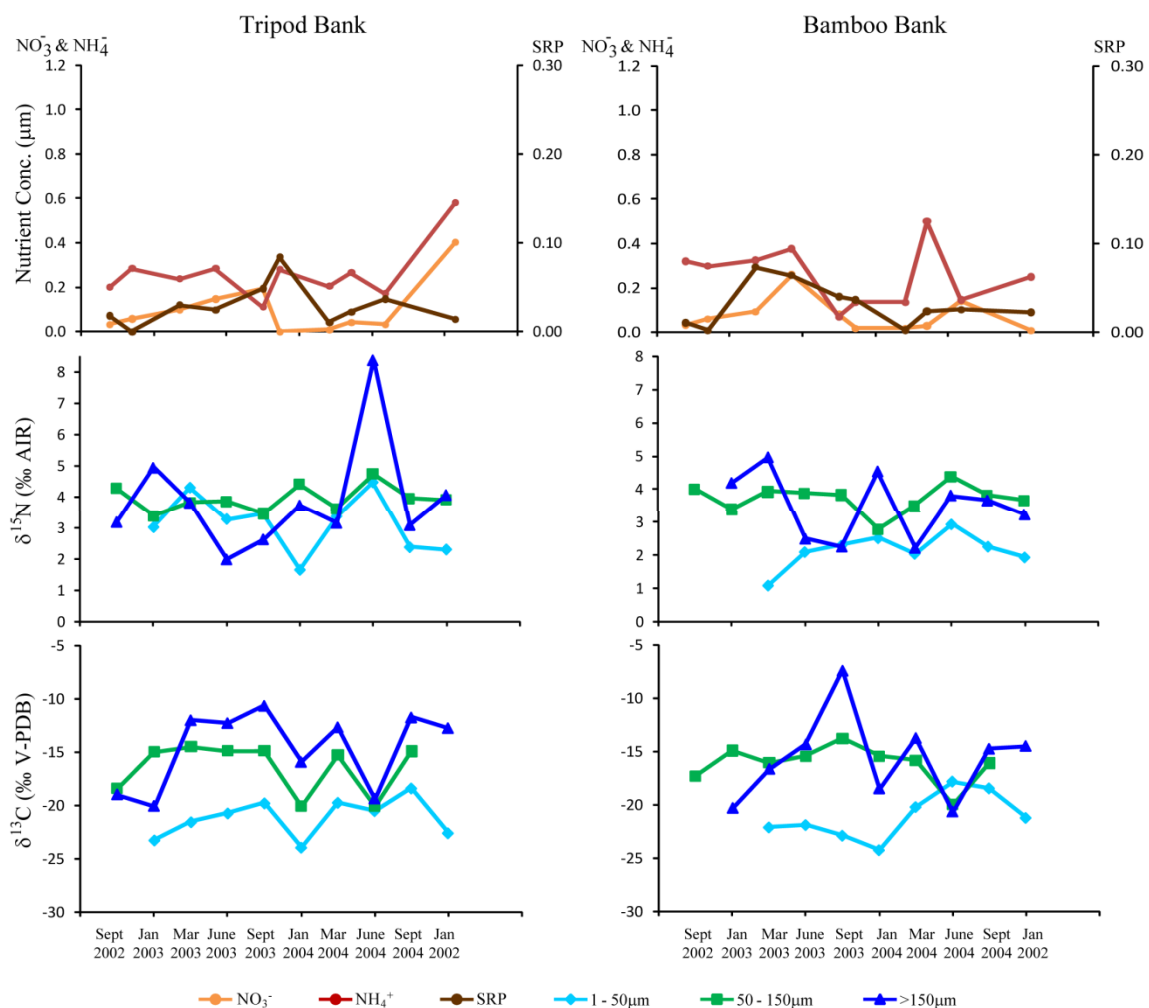


Figure 3.5 Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from shallow mudbank settings in Western Florida Bay. Nutrient concentration data (nitrate, ammonium, and soluble reactive phosphorus) are also shown.

values shown in the three successive January samplings, and more enriched signals apparent in the March and June sampling events. Carbon isotopic values in the 0.1-50 μm size class exhibited similar patterns of January at these two banks; however, the trend was less clear in the 50-150 μm size class. Sprigger Bank POM isotopic trends were more complicated than those seen at nearby sites. Annual patterns were more ambiguous, though still present, and slightly out of phase with patterns seen in the Middle Keys and other Western Florida Bay sites. The most depleted nitrogen isotopic values

were found repeatedly in September sampling intervals, with more enriched signatures observed in March and June quarters.

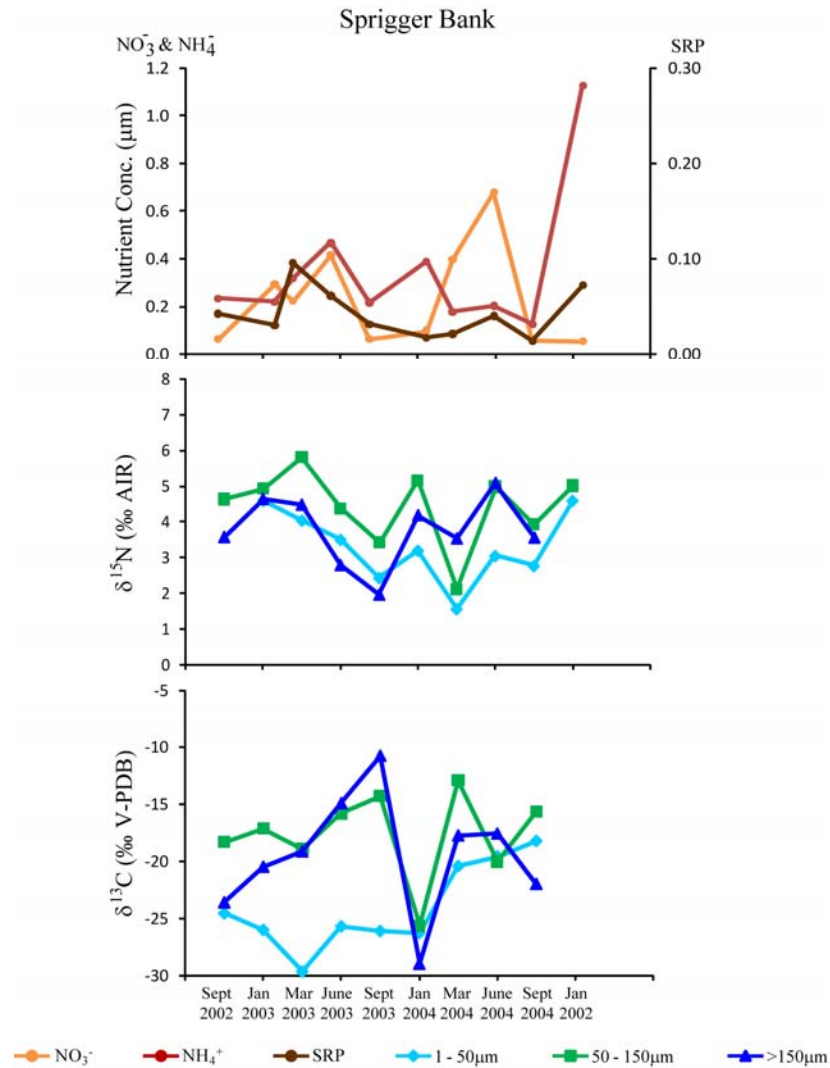


Figure 3.6 Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from a shallow mudbank setting in Western Florida Bay. Nutrient concentration data (nitrate, ammonium, and soluble reactive phosphorus) are also shown.

The central (Bob Allen Bank) and northeastern (Duck Key) Florida Bay sites time-series are shown in Figure 3.7, exhibiting the most pronounced seasonal nitrogen isotopic signal in spring isotopic enrichments and fall depletions in the phytoplankton size fractions. At Duck Key, a 4‰ depletion in $\delta^{15}\text{N}$ of the 50-150µm fraction in the Sept. 2004 sampling

was coincident with a large influx of inorganic phosphorus (SRP), however trends in other size fractions were more ambiguous. A similar, but smaller magnitude, depletion was found at Bob Allen Key with no concurrent changes in nutrient availability.

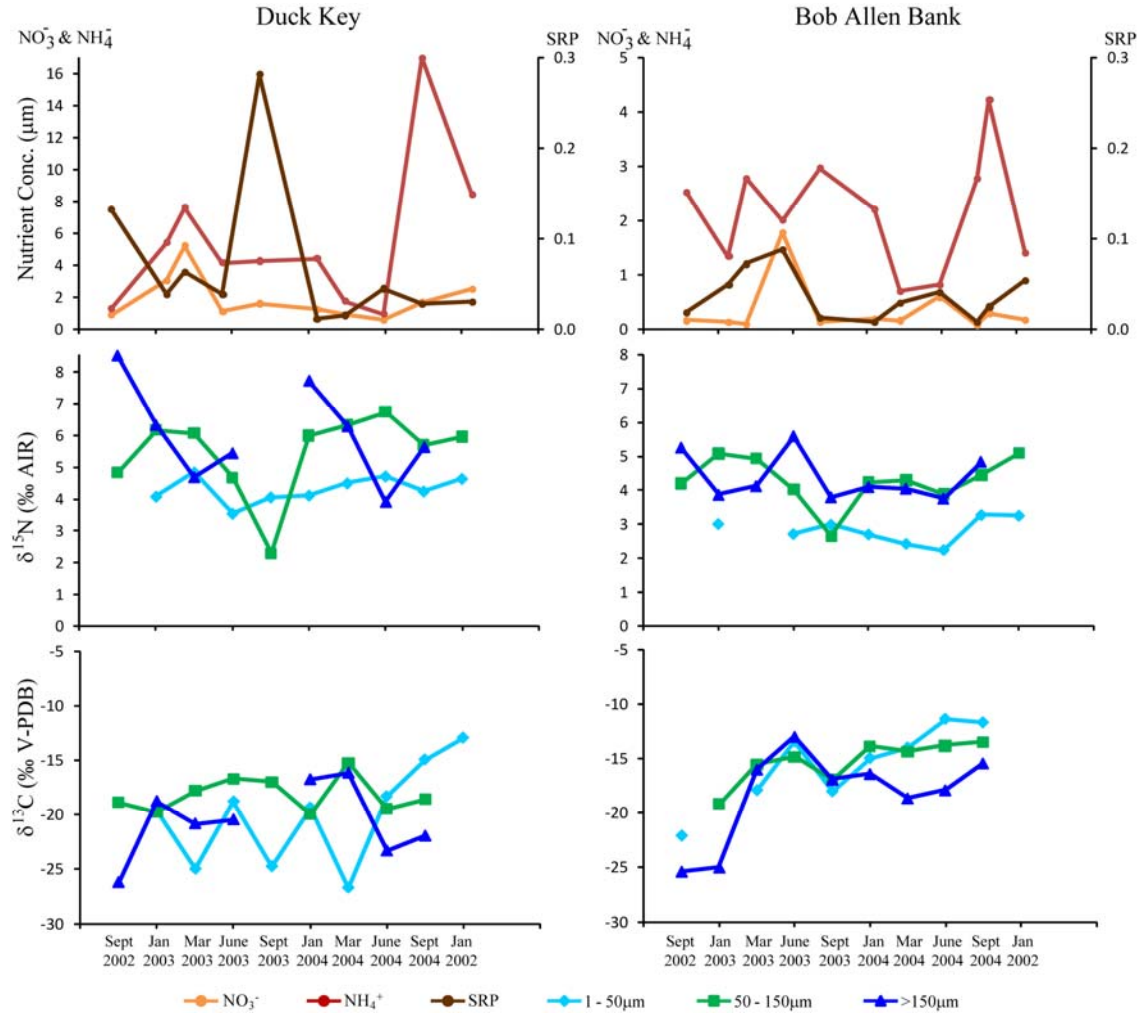


Figure 3.7 Time series of POM isotopic values ($\delta^{13}\text{C}$ & $\delta^{15}\text{N}$) from 3 size fractions collected quarterly over a two year period from shallow mudbank settings proximal to both islands and Everglades outflows in Northeastern and Central Florida Bay. Nutrient concentration data (nitrate, ammonium, and soluble reactive phosphorus) are also shown.

Figure 3.8 shows time series $\delta^{15}\text{N}$ data by month, combining the two years of samples collected in the 0.1-50 and 50-150 μm fractions to show average annual trends. Sites were grouped according to annual isotopic patterns. The Atlantic reef sites

(Carysfort Reef and Molasses Reef) exhibit nitrogen isotopic enrichment in January, with depletion in June. The Middle Keys Channels sites (Tennessee Reef, Coffins Patch Channel, Bahia Honda Channel, Tripod Bank, and Bamboo Bank) had depleted $\delta^{15}\text{N}$ values in January with isotopic enrichment evident in the spring and summer quarters. Florida Bay sites (Sprigger Bank, Bob Allen Bank, and Duck Key) showed a pattern of depletion in September with enrichment throughout the rest of the year.

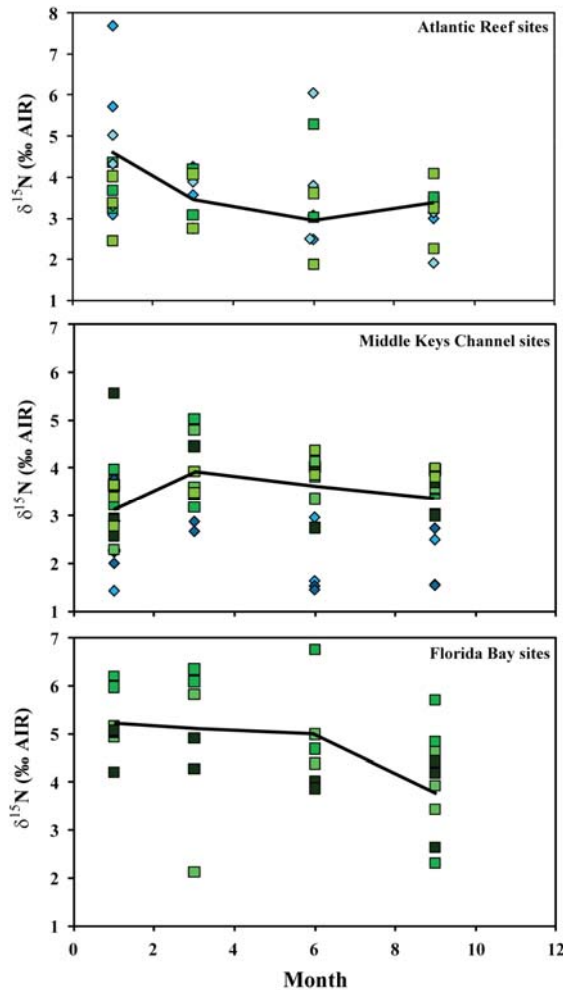


Figure 3.8 Mean annual patterns in $\delta^{15}\text{N}$ values; 2 years combined. Diamonds denote 0.1-50µm size fraction, squares denote 50-150µm size fraction. Atlantic Reef sites include Carysfort and Molasses Reef; Middle Keys channels include Tennessee Reef, Coffins Patch Channel, Bahia Honda Channel, Tripod Bank and Bamboo Bank; Florida Bay includes Sprigger Bank, Bob Allen Bank, and Duck Key.

While there appeared in many instances to be relationships between site-specific nutrient parameters and isotopic values, only one site, Duck Key in Northeastern Florida Bay, exhibited statistically significant correlations between nutrient concentration and isotopic composition. At Duck Key, salinity was found to be positively correlated with $\delta^{15}\text{N}$ in the 50-150 μm size fraction ($R = 0.713$; $p = 0.02$) and negatively correlated with the >150 μm size class ($R = -0.788$; $p = 0.02$). $\delta^{15}\text{N}$ of the 50-150 μm fraction from Duck Key was also negatively correlated with phosphorus concentrations (SRP) ($R = -0.891$; $p < 0.001$). There were no statistically significant correlations between two-year datasets of water quality parameters and isotopic compositions of POM and the remaining sites.

3.4.2 Size Class Variability

Differences between POM size fractions in nitrogen and carbon isotopic values are illustrated in Figures 3.9 -3.11. With a few exceptions, there was a trend of isotopic enrichment with increasing size fraction. Results of one-way ANOVA tests comparing size classes within each sampling location are summarized in Table 3.3.

Table 3.3 Differences between size fractions: ANOVA P-Values

Site	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰PDB)	Molar C:N
Carysfort Reef	0.475	0.099	0.533
Molasses Reef	0.204	0.003 <i>ab, ac</i>	0.01 <i>ab, bc</i>
Tennessee Reef	0.142	0.014 <i>ab, ac</i>	0.533
Coffins Patch Channel	0.001 <i>ab, ac, bc</i>	0.003 <i>ab, ac</i>	0.607
Bahia Honda Channel	0.001 <i>ab, ac</i>	0.111	0.287
Tripod Bank	0.089	0.001 <i>ab, ac</i>	0.004 <i>ac, bc</i>
Bamboo Bank	0.003 <i>ab, ac</i>	0.003 <i>ab, ac</i>	0.95
Sprigger Bank	0.066	0.012 <i>ab, ac</i>	0.485
Bob Allen Bank	0.001 <i>ab, ac</i>	0.175	0.024 <i>ab, ac</i>
Duck Key	0.014 <i>ab, ac</i>	0.325	0.068

*Significant P-values are shown in bold, specific pairwise differences are denoted: *a* 0.1-50 μm ; *b* 50-150 μm ; *c* >150 μm .

Significant differences were identified at several stations, however, differences in $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ were not necessarily coincident, indicating decoupling between carbon and nitrogen cycling reflected in POM isotopic values. $\delta^{15}\text{N}$ values increased significantly with particle size class at half of the study sampling locations; Coffins Patch Channel (site 248), Bahia Honda Channel (site 255), Bamboo Bank (site 287), at Bob Allen Bank (BA) and at Duck Key (DK). At Coffins Patch Channel, there were significant differences between all fractions, with a 1‰ enrichment with each size class increase, however at the remaining locations only the 0.1-50 μm fraction was significantly depleted (by 1.1 to 1.6‰ depending on site, see Table 3.1) in nitrogen isotopic composition relative to both the 50-150 μm and >150 μm fractions, while the larger two fractions did not differ from one another. In terms of $\delta^{13}\text{C}$, relationships between size fraction isotopic compositions show much higher variability with less consistent trends, yet significant increases in isotopic enrichment with particle size were evident at Molasses Reef (225), Tennessee Reef (243), Coffins Patch Channel (248), Tripod Bank (284), Bamboo Bank (287), and at Sprigger Bank (SP). Carbon isotopes of all size fractions significantly differed at both Molasses Reef and Tennessee Reef, showing 5‰ and 2‰ enrichments across the size classes, respectively. At the remaining sites, comparable with $\delta^{15}\text{N}$ differences, the 0.1-50 μm size class was significantly depleted relative to the larger fractions, yet the 50-150 μm and >150 μm fraction did not differ significantly from one another. The relationship between size fraction samples and bulk POM samples is shown in Figure 3.11. The nitrogen isotopic composition of the three size fractions collected in a given sampling event are shown along with a single bulk sample.

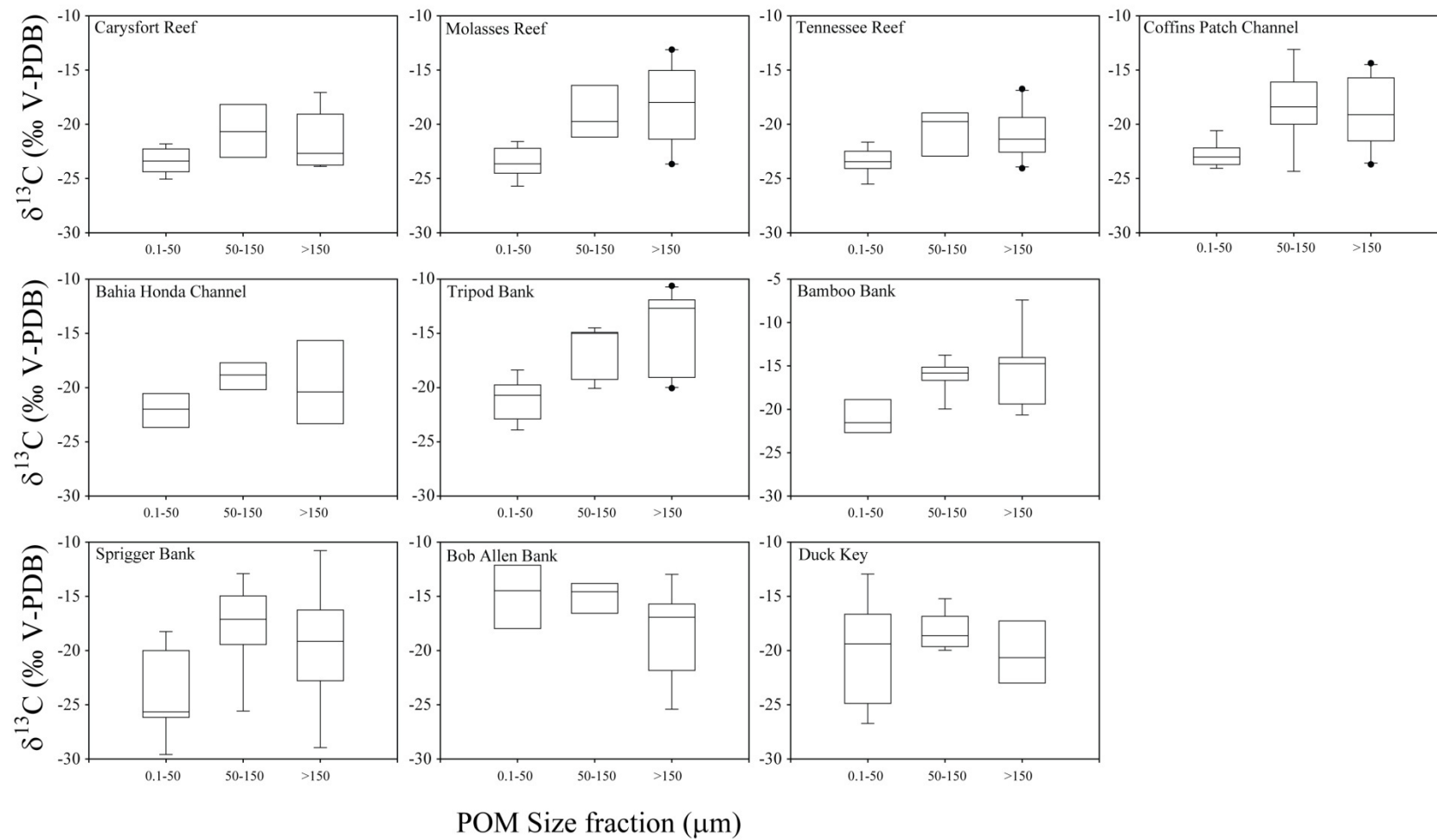


Figure 3.9 Variation in $\delta^{13}\text{C}$ between POM size fractions combining ten sampling intervals. Box plots show median, upper and lower quartiles, and data extremes over 10 sampling intervals in the three size fractions.

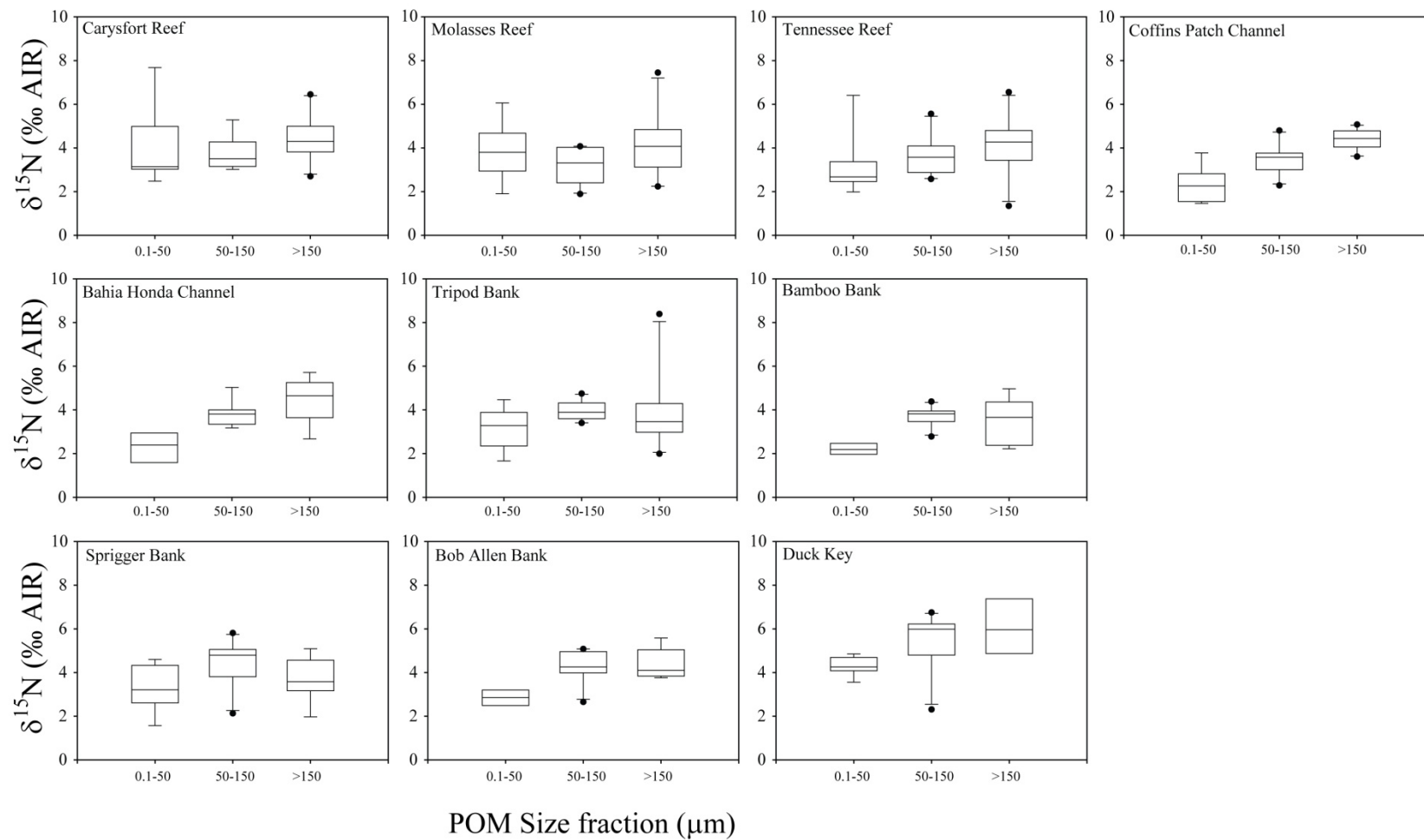


Figure 3.10 Variation in $\delta^{15}\text{N}$ between POM size fractions combining ten sampling intervals. Box plots show median, upper and lower quartiles, and data extremes over 10 sampling intervals in the three size fractions.

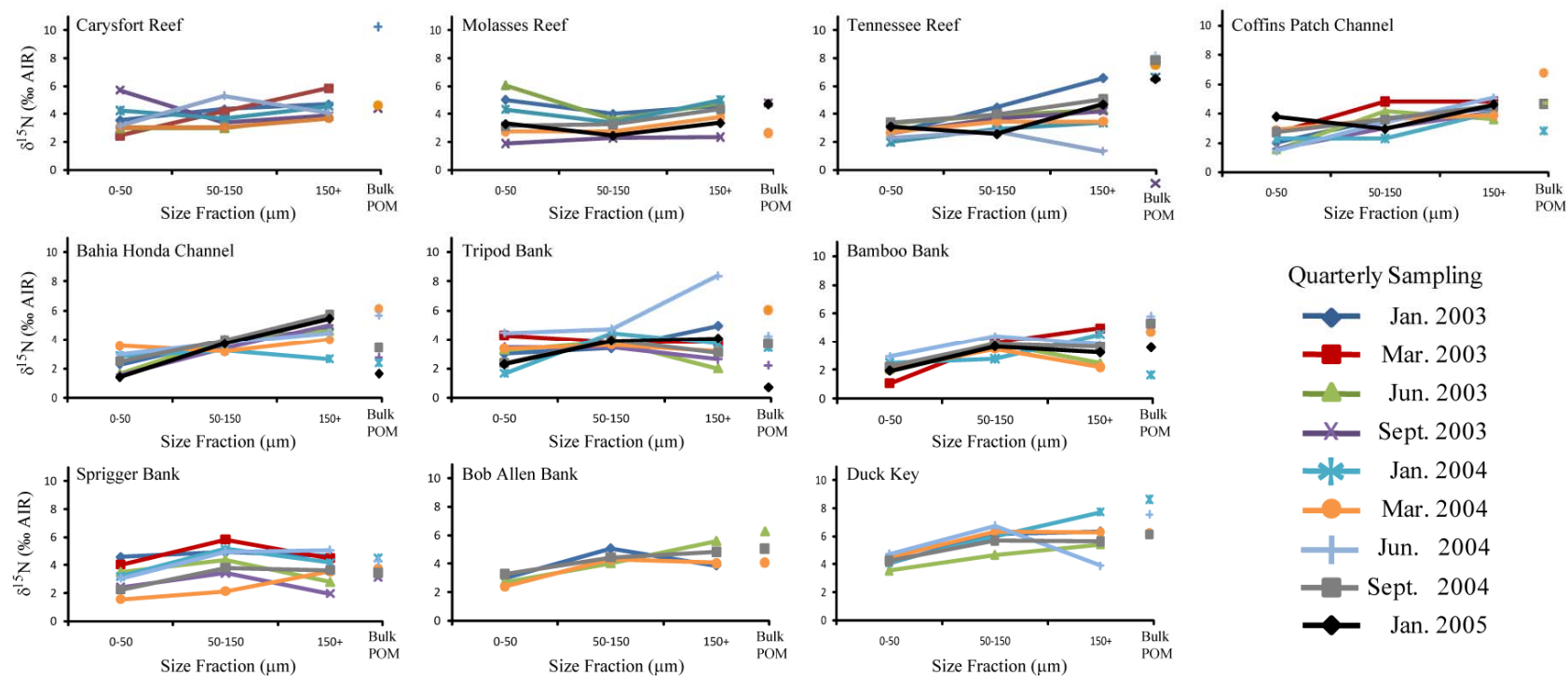


Figure 3.11 Variation in $\delta^{15}\text{N}$ between POM size fractions during individual sampling intervals. Bulk samples corresponding to sampling periods in 2004 are shown with symbols on the right margin of each plot.

Differences between bulk POM $\delta^{15}\text{N}$ compositions and the size fractionated dataset vary by station and by sampling interval with no consistent pattern evident. In some samples, the bulk isotopic values were similar to one or more of the corresponding size fraction samples; in other samples, bulk isotopic compositions appeared to reflect an average of the three fractions; yet in still other samples bulk values were completely inconsistent with the size fraction data. Inconsistency between amalgamated versus size separated samples demonstrates the high levels of heterogeneity in mixed bulk samples. Any particle of anomalous isotopic composition will control the overall isotopic composition measured.

Isotopic values among different sampling locations separated into individual size classes (e.g., cross-site comparisons of all $\delta^{15}\text{N}$ or $\delta^{13}\text{C}$ from the 0.1-50 μm fraction) showed significant differences among sites in both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$. However, pair-wise comparisons isolating differences demonstrated that Duck Key, in Northeastern Florida Bay, differed significantly from all other sites in terms of $\delta^{15}\text{N}$ at both the 50-150 μm and >150 μm size levels; however, all other specific differences in isotopic composition by specific size fractions can be categorized as differences between site groups “Florida Bay” versus “Atlantic Ocean”. The trends separating Bay and Ocean sites in all size classes are shown in bivariate isotope plots (Figure 3.12). In the 0.1-50 μm fraction (Figure 3.12A) there was much higher variability in $\delta^{13}\text{C}$ values from the Florida Bay sites, whereas the Ocean sites showed higher variability in $\delta^{15}\text{N}$. Carbon and nitrogen isotopic values were not however significantly correlated in either Bay or Ocean sites in the smallest size class. In the 50-150 μm size class (Figure 3.12B), Florida Bay sites

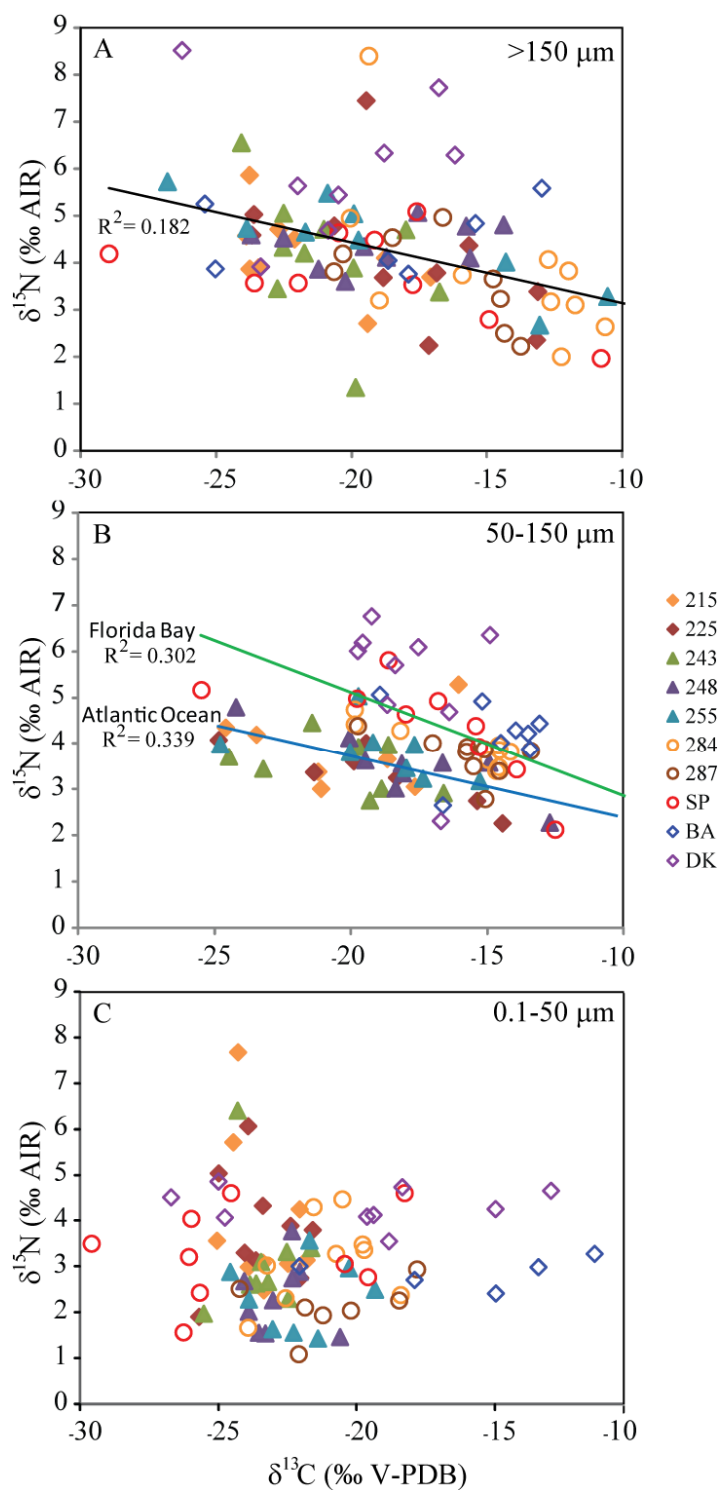


Figure 3.12 Bivariate isotope plots of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ for the three size fractions. A: >150 μm B: 50-150 μm C: 0.1-50 μm . Open symbols denote Florida Bay sampling sites, closed symbols represent Atlantic Ocean sites.

clearly have more enriched $\delta^{15}\text{N}$ than Ocean-side sites but the differences in both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values between Bay and Ocean groups were statistically significant ($p < 0.001$). Further, carbon and nitrogen values showed significant negative correlations in both groups with Bay and Ocean correlation coefficients (Pearson R-values) of -0.549 and -0.582 respectively, both significant at the $p < 0.001$ level. Figure 3.12C illustrates that there was no significant difference in $\delta^{15}\text{N}$ between Bay and Ocean site groups in the $>150\mu\text{m}$ size fraction; however, $\delta^{13}\text{C}$ values were significantly different ($p < 0.05$). Carbon and nitrogen isotopic values were also significantly correlated in this size fraction, demonstrating correlation coefficients of -0.457 and -0.443 in Bay and Ocean-side groupings, respectively.

3.4.3 Source indicators of POM

Bivariate plots comparing isotopic and molar C:N ratio values are shown in Figure 3.13. There was no linear relationship relating either $\delta^{15}\text{N}$ or $\delta^{13}\text{C}$ to C:N ratio however differences between size fractions and between Florida Bay and Atlantic Ocean site pools are evident. Values for the C:N ratios of the different size classes ranged from 0.84 – 53.8, however the majority of values were less than 30. The 0.1-50 μm size class were clustered with C:N values < 10 with both Florida Bay and Atlantic Ocean site pools. The 50-150 μm fraction demonstrated a broader range in C:N values, still with large proportion in the 5-10 range, but with a significant number of samples falling between 10 and 30. The distinction between Florida Bay and Atlantic Ocean site pools is apparent, with the Florida Bay values showing a wider range in both isotopic values and C:N ratios. The $>150\mu\text{m}$ fraction exhibited a range in values similar to the 50-150 μm size class, and

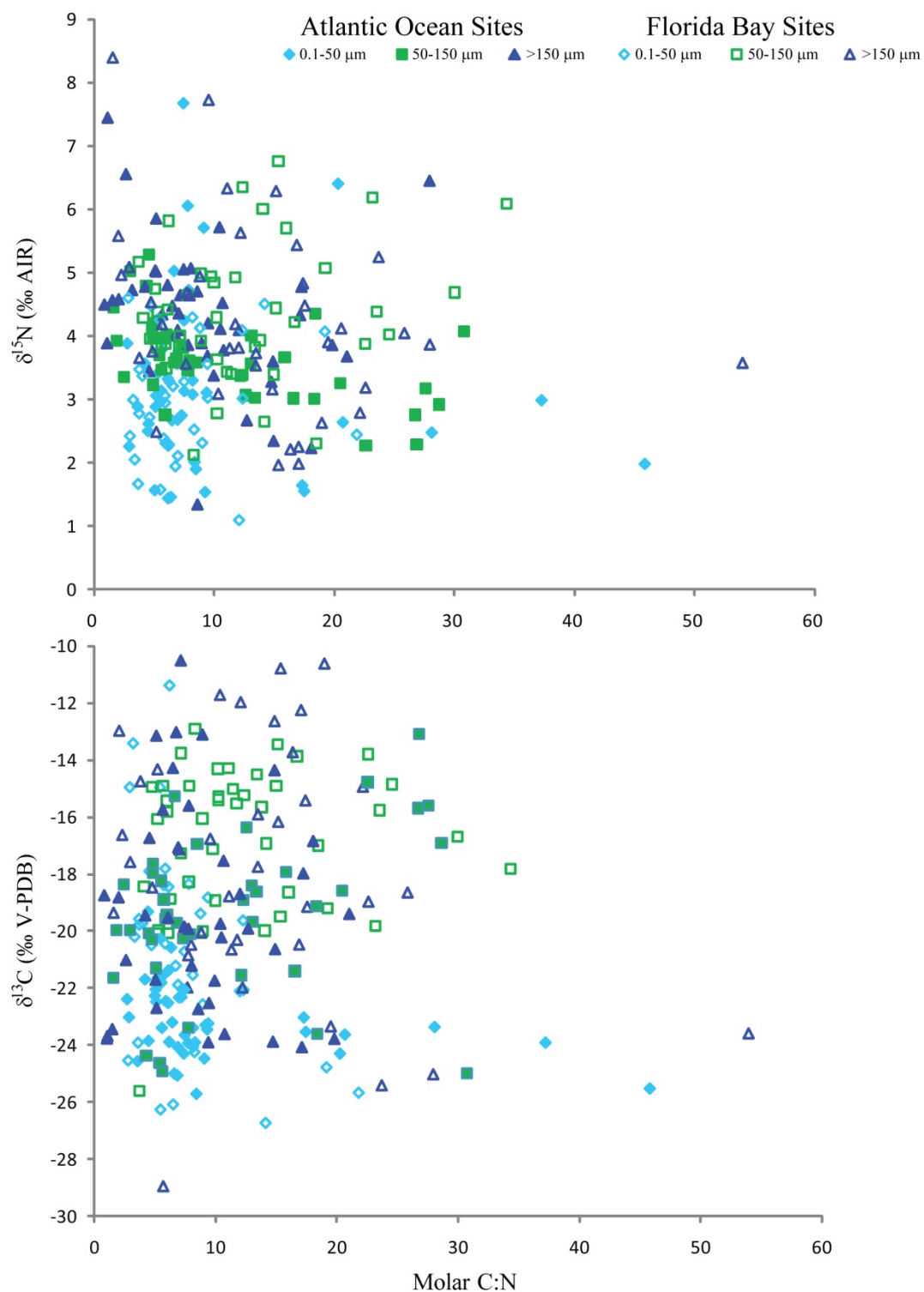


Figure 3.13 Bivariate plots of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ with Molar C:N ratio for the three size fractions. 0.1-50 μm is shown with diamonds, 50-150 μm is shown with squares, >150 μm is shown with triangles. Open symbols denote Florida Bay sampling sites, closed symbols represent Atlantic Ocean sites.

also showed a similar trend toward more dispersed values in the Florida Bay pooled sites in terms of both isotopic and molar C:N ratio values.

Figures 3.14 and 3.15 display populations of eukaryotic algae and cyanobacteria from the 0.1-50 μ m size fraction in flow cytometry analysis panes. Figure 3.14 shows sampling intervals from 2004 from the Atlantic Ocean sites, whereas Figure 3.15 depicts populations at the Florida Bay locations over the same period. Each point on the individual plots represents a single particle detection, thus darker areas indicate higher particle densities. A high degree of spatial and temporal variability is evident between sites and over the course of the four quarterly sampling intervals shown with large populations of *Synechococcus* sp., *Prochlorococcus* sp., and likely other cyanobacterial groups fluctuating in abundance over time. Eukaryotic algae are always present at much lower abundances than the cyanobacterial populations, yet also show variation in abundance over time.

3.5 DISCUSSION

Several studies of seasonal isotopic changes in size fractionated particulate organic material have demonstrated high levels of temporal variability. Wainright and Fry (1994) documented seasonal variation in POM- $\delta^{13}\text{C}$ of $>6\text{‰}$, while $\delta^{15}\text{N}$ variability was $>5\text{‰}$ in coastal New England over the course of two summer phytoplankton bloom periods. Seasonal variations measured in size fractionated POM from the Baltic Sea were of a similar magnitude, showing overall seasonal change of 5-7 ‰ through the course of the summer productivity season (Rolff 2000). Sato et al. (2006) illustrated even larger

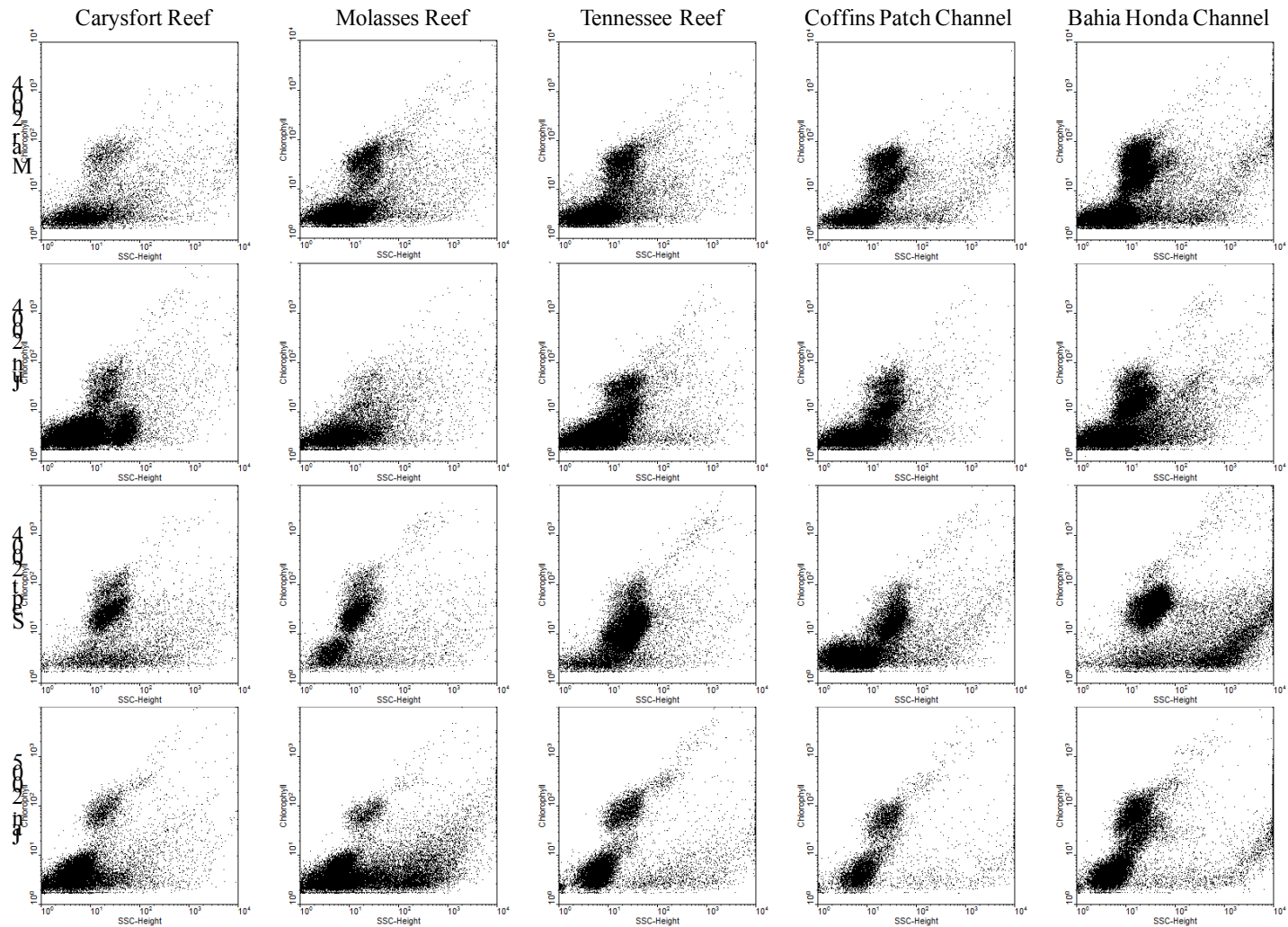


Figure 3.14 Flow cytometry analyses of Florida Keys Reef Tract phytoplankton collected quarterly at 5 stations along a N-S transect down the Florida Keys. 50 000 events are displayed after acquisition in log mode. Chlorophyll-*a* autofluorescence is plotted against side angle light scatter.

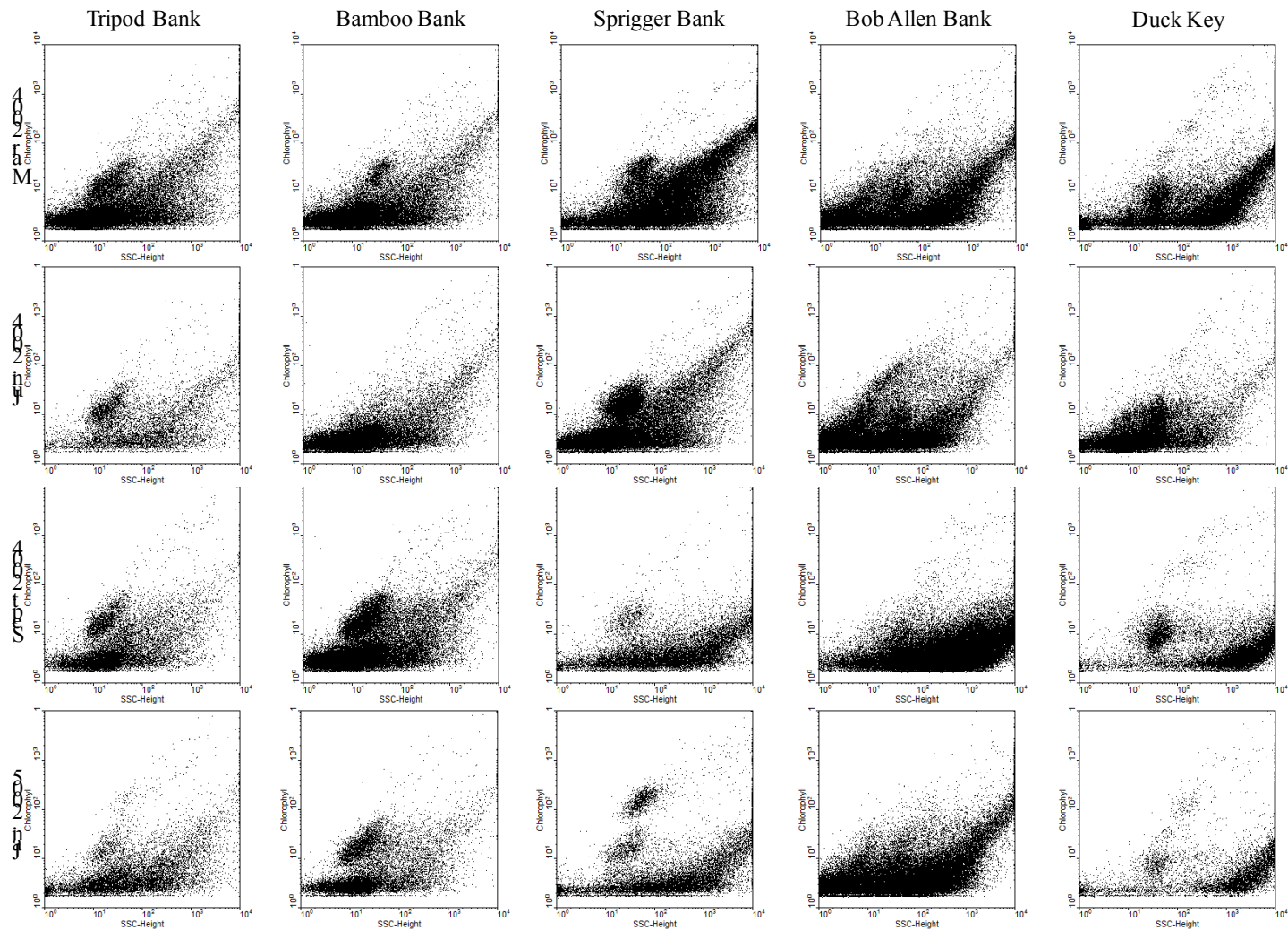


Figure 3.15 Flow cytometry analyses of Florida Bay phytoplankton collected quarterly at 5 stations in the bay. 50 000 events are displayed after acquisition in log mode. Chlorophyll-*a* autofluorescence is plotted against side angle light scatter.

isotopic fluctuations on a seasonal basis in Tokyo Bay, with both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values changing by up to 10‰ between winter and spring. All of these studies took place in temperate coastal environments with much higher seasonal variation in parameters such as temperature than the seasonal differences seen over the course of the year in South Florida, yet here we found seasonal fluctuations in POM isotopic composition of equal or greater magnitude. The $\delta^{13}\text{C}$ values varied quarterly in Florida Bay sites by up to 20‰ with an average range of 8.46‰ across all size classes and sites measured. Nitrogen isotopic values exhibited annual fluctuations of up to 6.4‰ with an average range of 3.0‰ across all sites and size fractions. These variations are larger than the seasonal variation measured over a period of eight years in South Florida seagrass communities. The average seasonal change in the regionally dominant seagrass, *Thalassia testudinum*, is under 1‰ in terms of $\delta^{15}\text{N}$ and less than 2‰ in $\delta^{13}\text{C}$ (Fourqurean et al. 2005, Anderson and Fourqurean 2003).

Similar to the results presented here, Xu and Jaffé (2007) showed large differences in organic biomarker proxies from POM samples distributed across Florida Bay and also between wet and dry seasons, indicative of changes in POM sources on both spatial and temporal scales. The high variability evident in the isotopic signature of POM from the South Florida coastal zone has significant geochemical implications. Isotopic values are often applied in food-web studies that examine basal trophic levels or trace carbon flow in various environments. Inadequate understanding of the variability of POM isotopic values undermines the assumptions upon which such studies are based. Nitrogen isotopic variability has been invoked as a recorder of anthropogenic sewage pollution in the coastal zone (Lapointe and Clark 1992, Lapointe et al. 2004, Ward-

Paige et al. 2005, Lapointe et al. 2005); however, values of $>8\text{‰}$ were recorded in this study in areas far from anthropogenic sewage sources, with a very low likelihood of such contamination. Furthermore, studies examining water column and water-sediment interface nitrogen cycling processes such as denitrification and nitrification often utilize bulk POM isotopic measurements to examine evidence of nitrogen recycling. The high levels of variability in isotopic signals over the two year period examined here suggests that annual variations must be taken into account in order to accurately apply isotopic data to evaluate ecological and geochemical processes.

3.5.1 Temporal variability and hydrodynamic regime

Within the large range of isotopic values measured for POM through the course of this two-year dataset, is a high level of spatial heterogeneity observed in quarterly trends. The studies of Wainright and Fry (1994), Rolff (2000), and Sato et al. (2006) were all limited in scope to a few (1-3) sampling stations in their respective localities, which were then taken to be representative of the local coastal system. In the dynamic coastal system of South Florida, even sampling locations close to one another may show significant variability in absolute isotopic values and in the seasonal patterns exhibited in those values over time. Both the northern Key Largo reef sites showed isotopic enrichments in successive January sampling events with ensuing isotopic depletions in June samples. Sites in the Middle Keys sites, Tennessee Reef, Coffins Patch Channel, and Bahia Honda Channel, while still located along the Florida Keys Reef Tract, exhibited the opposite trend, with depleted isotopic values in both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ observed in January while enriched values were measured in summer quarter samples. In fact, the Middle Keys

sites exhibited annual trends more similar to those at Western Florida Bay sites than to the more northern Key Largo reef sites. By far the greatest isotopic variability was found in the axial Florida Bay transect sites, Duck Key, Bob Allan Bank, and Sprigger Bank, which also exhibited quarterly trends out of phase with all other sites. Whereas the other site groupings showed variability between summer and winter samplings (January versus June), the Florida Bay sites showed the most significant depletions in the fall sampling intervals.

All of the differences in POM isotopic trends observed may be understood in terms of hydrodynamic regime at different areas in the south Florida coastal zone (Figure 3.16). The northern reef sites are located offshore of one of the longest land stretches in the Florida Keys – Upper Key Largo, and so have limited connectivity with the adjacent Florida Bay system. Nutrient sources to the Florida Keys reefs have been the subject of ongoing study (Leichter et al. 2008, Leichter et al. 2007, Leichter et al. 2003, Lapointe and Clark 1992, Lapointe et al. 2005 and others) and it has been well established that high frequency tidal upwelling represents a significant widespread, yet episodic, source of high nitrate and phosphate fluxes on Florida Keys Reef slopes. A significant pool of dissolved nutrients exists below the thermocline seaward of the Florida Keys Reef Tract (Lee et al. 1994 reported subthermocline nitrate concentrations of 3-15 μ M off the southern Florida Keys), and this transiently upwelled nutrient source impacts the reef crest environment and may be advected into back reef environments (Lee et al. 1994, Leichter et al. 2003, Smith et al. 2004). Episodic upwelling has been shown to be a predominantly summer phenomenon, when stratification at the thermocline is most pronounced as surface temperatures increase (Leichter et al. 2003). The isotopic

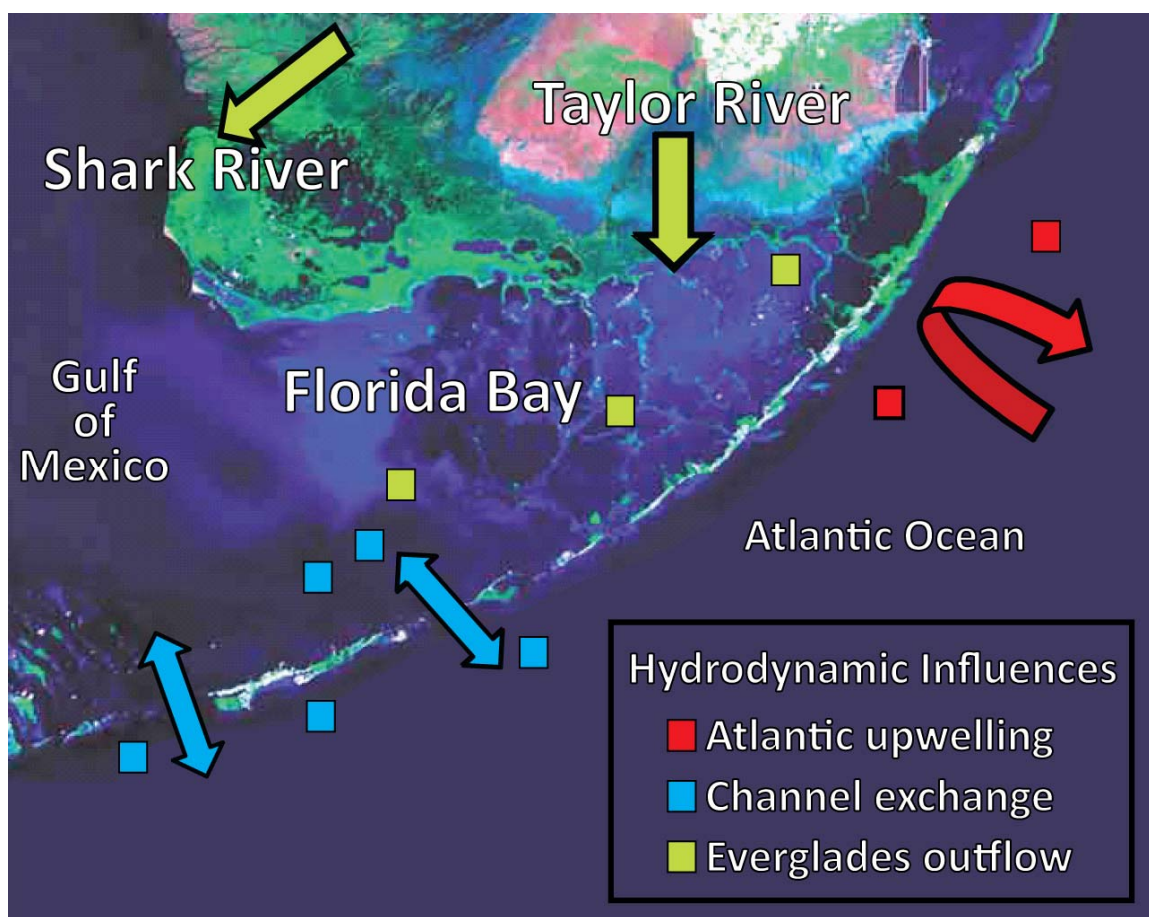


Figure 3.16 Conceptual model illustrating the distribution of South Florida coastal hydrodynamic zones as they influence nutrient dynamics and POM isotopic composition over time.

depletion trends evident in June sampling intervals at the northern reef sites correspond to increased SRP and DIN availability and also to increased population densities in cyanobacteria (Figure 3.14). Higher levels of DIN become available during the summer in the reef zone due to deeper water upwelling events and this influx of nutrients supports higher cyanobacterial densities, which in turn have been shown to fractionate carbon isotopes to a higher degree than other marine planktonic organisms (Wainright and Fry 1994). Additionally, under the nutrient replete conditions furnished by upwelling events, nitrogen isotopic fractionation could be expected to alter the $\delta^{15}\text{N}$ of the upwelled nitrate during assimilation processes, producing POM isotopic values of 2-3‰ as seen in the

summer isotopic depletions ($^{15}\text{NO}_3^-$ measured seaward of the Florida Keys Reef Tract (Leichter et al. 2007) exhibits $\delta^{15}\text{N}$ values of 3.5-5.5‰). Similar isotopic values have been observed in deep water algal samples known to be influenced by the same sub-thermocline nutrient sources (Leichter et al. 2008).

The Middle Keys sites, Tennessee Reef, Coffins Patch Channel, and Bahia Honda Channel are located proximal to large channels crossing the Florida Keys (Channels 2 and 5, and Moser Channel/Seven-Mile Bridge). The channels connect these sites to the western Florida Bay sites at Tripod and Bamboo Banks. Exchange of water through tidal channels connecting the Gulf of Mexico and Atlantic sides of the Florida Keys is an important feature of the regional circulation (Smith 1998, Gibson et al. 2008). Gibson et al. (2008) demonstrated a net discharge of water and nutrients through Long Key Channel from Florida Bay to the Florida Keys National Marine Sanctuary; thus it is unsurprising that POM sampled on either side of such transport channels would be related in terms of geochemical characteristics and temporal variations. The channel sites all show marked differences from the outer reef sites, with depleted isotopic values evident in both carbon and nitrogen in January sampling intervals, and enriched summer signals observed in successive June samplings. More than one factor may influence these fluctuations. First, flow cytometry analyses (Figure 3.14, Tennessee Reef and Bahia Honda Channel) reveal much lower concentrations of detritus material in samples collected in January, and fairly pure cyanobacterial populations in these samples. While the isotopic values are not sufficiently depleted to demonstrate nitrogen fixation as a dominant process, high levels of cyanobacteria may be related to some level of nitrogen fixation, as shown in previous studies (Evans et al. 2006, Glibert et al. 2004, Philips and Badylak 1996). Alternatively,

enriched nitrogen isotopic values at the channel-associated sites in spring and summer sampling events may reflect surface nutrient utilization, as these time periods exhibited much higher population densities of cyanobacteria (Figure 3.14) in the 0.1-50 μ m size fraction and of diatoms in the 50-150 μ m size fraction. While it is possible that the cyanobacteria populations evident could contribute some or all of their nitrogen requirements through the N-fixation metabolic pathway, coincident diatom populations are not capable of generating bioavailable nitrogen through fixation and thus are dependent on surface nutrient availability. Western Florida Bay is at the nitrogen-limited end of the nitrogen-phosphorus limitation gradient (Boyer et al. 1997). Under high primary productivity conditions, classic Rayleigh fractionation with depletion of surface nutrient pools would lead to gradual isotopic enrichment in both residual nutrient pools and in planktonic algae subsequently accessing these pools during photosynthesis.

The axial Florida Bay sites, Sprigger Bank, Bob Allen Bank, and Duck Key, display the most variable quarterly isotopic changes, with $\delta^{15}\text{N}$ ranges of up to 4‰ and $\delta^{13}\text{C}$ ranges of up to 20‰. While the 20‰ change in $\delta^{13}\text{C}$ likely reflects a transient contribution of terrestrial organic material at Sprigger Bank, 10‰ variations were seen in all three Florida Bay sites. Florida Bay annual trends in POM isotopic values differed from the other hydrodynamic regions discussed above. Rather than enrichment-depletion trends occurring in January or June, The Florida Bay sites showed repetitive $\delta^{15}\text{N}$ depletions in the fall/September sampling intervals. At Sprigger Bank this depletion trend was evident in all size classes, whereas at the other more northeastern sites, the trend was exhibited only by the 50-150 μ m phytoplankton size fraction. The depletion

trend was most pronounced at Duck Key, the most northeasterly location, proximal to the Taylor River discharge from the Everglades, suggesting that this site might be significantly influenced by wet-season storm events, or by pre-storm freshwater discharge through Everglades flood control structures modulated by the South Florida Water Management District. The northeast subregion of the Florida Bay receives approximately 75% of the direct freshwater runoff to the bay through a series of small creeks draining Taylor Slough (Lee et al. 2008). Most of this runoff is retained within the region due to weak interbasin exchange that is largely controlled by local east-west wind forcing (Nuttle et al. 2000, Lee et al. 2008). It is not unexpected then that this region, with a much longer water residence time than other areas of the South Florida coastal zone, should show anomalous isotopic trends. Although the trends are perhaps most apparent in the isolated Northeastern zone in Florida Bay, Shark River Slough discharge is carried by the Florida Loop Current along the western boundary zone of Florida Bay, crossing Sprigger Bank during this transport directly toward the middle Keys channels (Brand 2002). Thus freshwater outflow from Shark Slough may significantly impact and/or contribute particulates to the area surrounding Sprigger Bank.

3.5.2 POM isotopic variability and water quality parameters

The South Florida Coastal zone is partitioned by geomorphological features and varied current and freshwater flow regimes. Quarterly POM data support the importance of hydrodynamic regime in controlling geochemistry, with definite differences in temporal patterns between reef, channel, and Florida Bay locations. However, while this study yields a statistically valid description of seasonal changes in POM geochemical

attributes in the unique environments of Florida Bay and the Florida Reef Tract, it was less suited to correlative analyses between the isotopic cycles within or between the size classes, or between the size classes and various environmental parameters potentially affecting them. Correlation requires high frequency sampling and an evenly spaced representation along a given physical or chemical gradient. Cyclic phenomena such as seasonal productivity cycles and nutrient drawdown lead to high variability and chaotic patterns in bivariate phase plots, and correlations may be undermined by even small lags in variables and related responses (Rolff 2000, Savoye et al. 2003). Correlations may also be flawed if the driving mechanisms controlling isotopic variability, such as nutrient source and availability or primary productivity levels, are not constant throughout the year. Strong seasonal drivers may be isolated in space and time, particularly in a system with an extreme dichotomy between wet and dry season patterns of rainfall and nutrient delivery. As a result, there are few direct correlations among isotopic values in POM size classes and environmental parameters, even while ambient seasonal nutrient availability does in fact exert influence over particulate isotopic composition.

In Northeastern Florida Bay, salinity and nutrient fluxes are largely controlled by seasonal Everglades outflows and direct rainfall inputs to the surface of Florida Bay itself (Nuttle et al. 2000, Rudnick et al. 1999, Boyer et al 1997), with modern water management practices favouring pulsed freshwater release during flooding stages (Rudnick et al. 1999), these drivers significantly affect isotopic signals in POM. This is the only region where statistical correlations between water quality and POM isotopic parameters were evident. Figure 3.7 shows a 4‰ negative excursion in the $\delta^{15}\text{N}$ value of the Duck Key phytoplankton associated size class (50-150 μm). This isotopic depletion is

coincident with a three-fold increase in ambient phosphorus concentration, and a two-fold increase in chlorophyll-*a* concentration, unaccompanied by any significant change in the concentrations of dissolved nitrogen species. SRP concentration has been cited as one of the dominant factors responsible for stimulation of cyanobacterial bloom events (Phlips and Badylak 1996, Glibert et al. 2004, Janssen et al. 2004). Previous studies have reported high abundances of the cyanobacterium genus *Synechococcus* in Northeastern Florida Bay (Evans et al. 2006, Lavrentyev et al. 1998, Philips and Badylak 1996), the most phosphorus-limited sector of the bay (Fourqurean et al. 1993, Boyer et al. 1997), supporting conclusions that this genus is an opportunistic phosphorus scavenger with euryhaline salinity tolerance (Stockner 1988). Depleted nitrogen isotopic values at both Duck Key in northeastern Florida Bay and also at Bob Allen Key in central Florida Bay in the September 2004 sampling suggest the potential for a phosphorus stimulated bloom originating in the northeast and being transported perhaps into central Florida Bay. *Synechococcus* has been shown to exhibit the capability for nitrogen-fixation (Phlips and Badylak 1996, Church 2005), so a mixture of POM containing both bloom organisms and particulates from more enriched sources could account for the 4 ‰ excursion found in this size fraction. Alternatively, with the pulse in phosphorus availability, a stimulated bloom would draw on the abundant inorganic nitrogen resources delivered in Everglades discharge. This inorganic nitrogen, postulated to originate from the upstream Everglades Agricultural area, might be isotopically light due to mineral fertilizer inputs.

3.5.3 Florida Bay versus Atlantic Ocean pooled site characteristics

Although there were few statistically significant correlations between water

quality parameters and POM isotopic values over time, there were significant differences between sites when entire isotopic time-series data sets were compared to one another. Inter-site differences were found in all POM size classes in both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ ($p > 0.001$) however, while Duck Key differed from all other sites ($p < 0.001$), other significant differences were rare and randomly distributed among site pairings, essentially reflecting the difference between Florida Bay and Atlantic Ocean sites in spite of apparent connectivity in seasonal patterns between Western Florida Bay and the Mid-Keys channel sites.

While correlation between carbon and nitrogen isotopic values pooled in Florida Bay versus Ocean sampling sites was not evident in all size fractions, the separation between Bay and Ocean POM was evident in each size class (Figure 3.12). In the 0.1-50 μm fraction, Florida Bay samples exhibited a wider range of $\delta^{13}\text{C}$ signatures, reflecting more estuarine inputs of particulate detritus from mangrove and seagrass organic material or an assemblage of cyanobacteria and picoplankton dependent on a broad range of decomposition product carbon sources. In this size fraction the ocean sites showed more restricted carbon isotopic compositions, with values characteristic of marine planktonic sources. In the 50-150 μm size class there was a significant negative correlation between carbon and nitrogen isotopic values, as well as a notable separation between Bay and Ocean sites. Florida Bay POM in this fraction was more enriched than that in the Ocean-side sites in terms of both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values. In the case of the $\delta^{15}\text{N}$, this is inconsistent with the contention that the Florida Keys Reef Tract is under the influence of anthropogenic sewage pollution related to the Florida Keys population (Lapointe and Clark 1992, Lapointe et al. 2004, Ward-Paige et al. 2005). These results support those of

Swart (2000) and Lamb (2006), in which extensive studies of nitrogen isotopic systematics along the Florida Reef tract showed no anomalous enrichments that could be unequivocally interpreted as evidence of sewage inputs to the reef setting. It is similarly unlikely that sampling locations along the central axis of Florida Bay were/are influenced by anthropogenic sewage contamination, yet the Florida Bay sites demonstrated a 3‰ enrichment over the pooled ocean sites. Duck Key showed the highest enrichments overall in nitrogen isotopic composition, which may reflect isotopic enrichment of nitrogen sources due to denitrification in anoxic mangrove sediments, which are then carried into Northeastern Florida Bay via Everglades freshwater discharge. With the exception of a few depleted Florida Bay samples, the ocean samples showed a wider range in $\delta^{13}\text{C}$ values, with a large number of values depleted by up to 6‰ relative to those found in Florida Bay.

Several early POM studies demonstrated a strong positive correlation between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ measurements on marine sedimentary particulates (Peters et al. 1978, Macko 1983, Wada et al. 1987). These correlations were interpreted as the result of mixing of terrestrial and marine organic matter, with terrestrial material having significantly more depleted isotopic values than marine material. The negative correlations evident in POM samples collected in the present study belie this simple mixing model in the South Florida coastal system. In addition, if terrestrial/marine organic matter mixing were to explain the isotopic variations observed, concurrent shifts would be observed in C:N ratios of the samples (with the terrestrial material contributing much higher C:N values), and a significant negative correlation between isotopic values and C:N ratios would be expected. In the present study, there was no significant

correlation between isotopic values and C:N ratios (Figure 3.13). In fact, very few samples contained organic material exhibiting C:N ratios characteristic of terrestrial organic matter. Most of the C:N ratios measured for the different size classes of POM were marine in character (<10), with a second grouping falling in the 10-30 value range, similar to the values measured for seagrasses (Fourqurean and Escorcia 2007). The separation between Florida Bay and ocean site POM was also evident in differences in C:N ratios, with the Florida Bay samples containing higher proportions of seagrass associated particles.

Further analysis comparing isotopic values to the logarithm of biomass (water column chlorophyll-*a*) demonstrated that the isotopic separation between Florida Bay and Ocean sites may be related to growth rates in the phytoplankton component of POM (Figure 3.17). Sato et al. (2006) illustrated that growth rate may be defined as the time-derivative of logarithmic Chlorophyll-*a*, finding significant positive correlations between this index of growth rate and the $\delta^{13}\text{C}$ values of POM. Their results suggest that decreases in isotopic discrimination or inducement of an HCO_3^- uptake mechanism are coincident with increases in growth rate (Sato et al. 2006). The 50-150 μm POM fraction observed in the present study also showed a significant positive correlation between $\delta^{13}\text{C}$ and Log Chl-*a* ($R = 0.324$, $p = 0.05$) in the phytoplankton size class (50-150 μm), implying a dependence of isotopic discrimination on growth rate. Furthermore, higher growth rates were coincident with more enriched values in both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, with the effect more pronounced in Florida Bay than at Ocean sites. The difference between Florida Bay and Ocean side sites reflects differences in species assemblages from the two

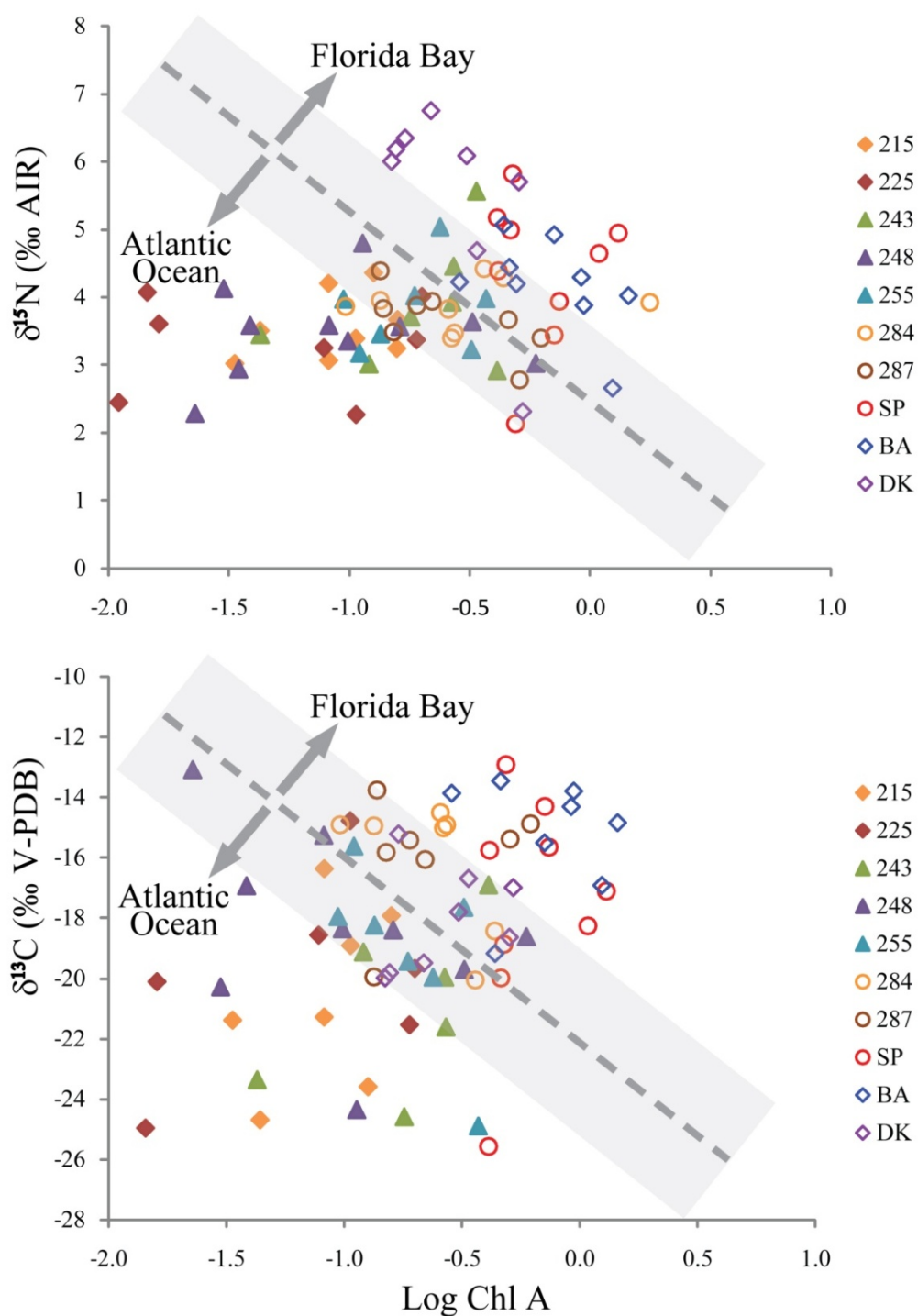


Figure 3.17 Bivariate plots of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ with Log Chlorophyll-*a* for the 50-150 μm size fraction, dominated by autotrophic diatoms and dinoflagellates. Open symbols denote Florida Bay sampling sites, closed symbols represent Atlantic Ocean sites. The grey zone represents overlap between the Atlantic Ocean and Florida Bay groups in isotopic POM characteristics; this zone includes the Middle Keys channel sites.

environments. Florida Bay 50-150 μ m was habitually dominated by a diverse diatom assemblage, with lower abundances of benthic foraminifera. Summer samplings documented a monospecific bloom of the dinoflagellate *Protoperidinium*, however this bloom was isolated at Bob Allen Bank. Atlantic Ocean sites, however, were predominately composed of dinoflagellates (dominated by several species of *Ceratium*) and both planktonic and benthic foraminifera (Appendix 4). The >150 μ m size class did not show as clear a separation between Florida Bay and Ocean site samples, although the Florida Bay group showed a number of values enriched in terms of $\delta^{13}\text{C}$, suggesting that some component of this size fraction is composed of seagrass detritus fragments.

These results, showing greater enrichments in both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in Florida Bay samples in comparison with Atlantic Ocean site samples, with variance in enrichments between individual size fractions of POM, agree broadly with concurrent seagrass isotopic time series. Nitrogen isotopic values in seagrasses from the same ocean sites vary between 0 and +6‰ over seasonal productivity cycles, while carbon isotopic values range between -12 and -7‰. Florida Bay seagrass $\delta^{15}\text{N}$ seasonal signals vary from -2 to +8‰, similar to the values seen in the POM. Seagrass carbon isotopic values do not show the same level of variation in comparison to the ocean sites as seen in the particulates, with values only showing slight enrichments relative to the ocean sites, ranging from -10 to -5‰ (<http://serc.fiu.edu/seagrass/!CDreport/DataHome.htm>).

3.5.4 Size fractionated sampling isotopic implications

During the second year of POM sampling detailed here, bulk POM samples were collected for comparison with size separated samples (Figure 3.11). It is clear that the

$\delta^{15}\text{N}$ values of bulk samples are highly susceptible to the influence of anomalous particles; in some comparisons, bulk values did not reflect those of any of the size classes, nor did they represent average values of combined size classes. Bulk filtered particulate samples from Lamb (2006) show carbon isotopic compositions that reflect a broad average of the $\delta^{13}\text{C}$ variation found among size fractionated POM isotopic data (Figure 3.17). However, $\delta^{15}\text{N}$ results from both this study and that of Lamb (2006) show that bulk samples exhibit a very wide range of variability that does not consistently return the average nitrogen isotopic composition of size differentiated samples. Clear understanding of POM components is essential to accurately interpreting data. Size fractionated sampling allows at least broad classification of assemblage composition, which must be taken into account, along with temporal sample variation, in order to accurately apply isotopic data in the evaluation of ecological and geochemical processes.

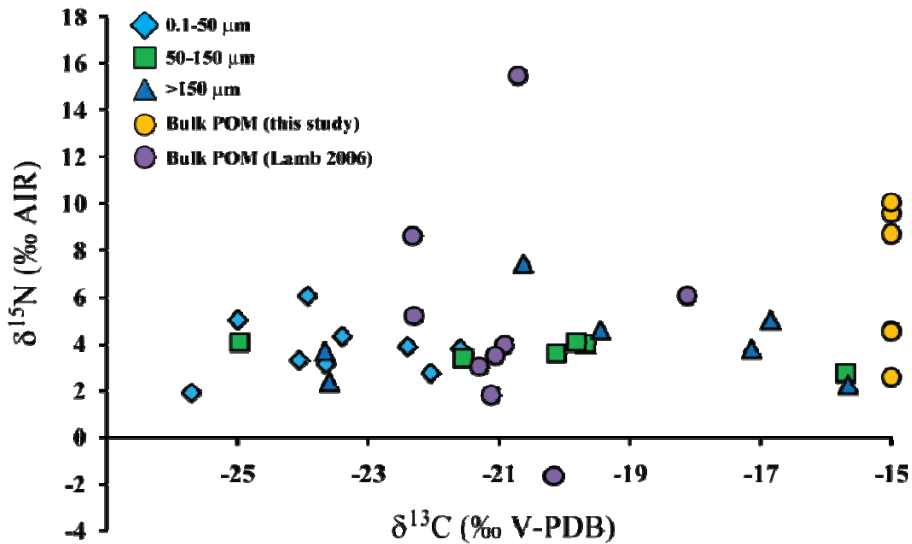


Figure 3.18 Isotopic values of size fractionated and bulk POM samples collected at Molasses Reef (this study) and Dixie Shoals (purple circles, Lamb 2006; collected in 2000-2002). Blue and green symbols represent size fractions and orange circles represent bulk samples collected concurrent with size fractions for $\delta^{15}\text{N}$ analysis only.

In both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values, and also in molar C:N ratios, there were significant differences between the values of the three size fractions of POM. Among all sites within the Atlantic Ocean and Florida Bay groupings, the 0.1-50 μm size fraction differed from both the larger size classes, the 50-150 μm and >150 μm fractions. However, the two larger size classes did not generally differ significantly from each other, apparently due to the higher level of variability that was evident in the two larger size fraction isotopic signatures. Relationships in isotopic values between POM size classes from each site in which all three size fractions were present during sampling are shown in Figures 3.8 and 3.9. For the most part, the 0.1-50 μm size class exhibited more depleted values than the other fractions in both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values. Similar relationships were found in other size-separated POM studies (Rau et al. 1990, Wainright and Fry 1994, Rolff 2000). Wainright and Fry (1994) suggested that cyanobacteria exhibit higher isotopic fractionation during carbon fixation than other organisms to account for the depleted values. This would also seem to be the case for the South Florida coastal system as cyanobacteria populations appear to dominate the smaller size fraction measured in this study. Most studies have found evidence of trophic enrichment between increasing size classes in POM (Rau et al. 1990, Wainright and Fry 1994, Rolff 2000, Sato et al. 2006). Based on previous work evaluating food chain length in the temperate coastal system, Wainright and Fry (1994) anticipated that 4 trophic levels should be evident in size class samples, and that ensuing enrichments of 4 and 12‰ would be evident in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ POM of increasing size fraction. This was determined not to be the case; although carbon isotopic values did show the expected enrichment with size fraction, nitrogen

isotopic values did not increase as significantly as anticipated. In the present study, maximum enrichments in terms of $\delta^{15}\text{N}$ values showed increases of approximately 5‰ across all size classes, with average increases of only 1.5‰ between adjacent size classes (Figures 3.9, 3.11). $\delta^{13}\text{C}$ enrichments across size classes exceeded enrichment factors associated with trophic enrichments, with differences of up to 10‰ evident between size classes. These differences are not explained by food-web relationships as traditionally understood in higher level producers and consumers, but by differences in carbon isotopic fractionation during species specific productivity in the 0.1-50 μm and 50-150 μm size classes, and are perhaps influenced by variations in the sources of particulate detritus which also represents a significant portion of each size class. Alternatively, Wainright and Fry (1994) postulated that isotopic selectivity/trophic enrichment associated with microbial carbon and nitrogen uptake and release may be very different from, and perhaps more variable than that observed in higher metazoan communities.

3.6 CONCLUSIONS

Despite the importance of POM in aquatic ecosystems, studies of POM are hindered by several methodological constraints. One of the most important is that POM is heterogeneous, consisting of living and dead cells, fecal pellets, marine snow aggregates, organically coated mineral grains, and other materials. Each of these different types of POM may have different temporal and spatial variations in chemical composition, as well as different cycling times and ultimate fates in aquatic ecosystems. Separating particulates on the basis of size does not alleviate difficulties inherent in

understanding the geochemical character of a variable mixture of particle sources, however size fractionation does allow some teasing apart of isotopic signal. This study has shown that there are significant differences among isotopic compositions of different size classes of POM, allowing a clearer understanding of particulate compositions and processes. Wide fluctuations were seen in seasonal patterns and in the responses of the separate size classes, indicating that composition of the size fractions is not simply a uniform amalgamation of detritus broken down to different particle sizes. Clearly planktonic communities respond to seasonal changes in environmental parameters, although driving mechanisms vary in space and time. In the case of the South Florida coastal zone, differences in all environmental parameters are dependent on the hydrodynamic regime of various areas in terms of geomorphological constraints and physical mechanisms of nutrient delivery and transport. Geochemical cycles in particulate organic material fractions reflect these patterns in hydrodynamic regime, showing seasonal patterns controlled by factors specific to particular zones of influence.

The level of spatial and temporal variability, variability between size classes, as well as differences between size fractionated and bulk POM samples have implications for current assumptions regarding the interpretation of bulk filtered POM samples as they are applied to understanding food-web studies, studies of organic matter sources to the coastal zone, and natural tracer experiments examining anthropogenic influences in the coastal environment. All these studies must take into account spatial and temporal changes in the stable isotopic composition of POM when interpreting relationships and patterns.

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CHAPTER 4

STABLE ISOTOPE COMPOSITION OF SEDIMENTARY ORGANIC MATTER FROM FLORIDA BAY

4.1 ABSTRACT

The shallow waters of Florida Bay represent an ideal environment for seagrasses, which are the most common benthic community in the region. Seagrass communities are, however, susceptible to a variety of anthropogenic disturbances, particularly changes in water quality. Environmental conditions in Florida Bay have become a concern due to recent increases in salinity, microalgal bloom frequency, and seagrass mortality. These changes have been attributed to 20th century decreases in freshwater discharge from the Everglades to Florida Bay, deteriorated water quality, and changes in exchange between the Bay and the Atlantic Ocean. In order to better understand environmental change over long time scales, sediment cores were collected in Summer 2002 from four locations in Florida Bay for multiple proxy analyses of seagrass abundance. Here bulk carbon and nitrogen stable isotope data are presented with sediment nutrient data from Trout Creek, Russell Bank, Bob Allen Bank, and Ninemile Bank.

The Trout Creek core, collected near the freshwater Everglades outflow of Taylor Slough had the most depleted average carbon isotopic value over time ($-19.64 \pm 0.62\text{‰}$) and the most enriched $\delta^{15}\text{N}$ values ($+5.65 \pm 0.059\text{‰}$). These values reflect higher inputs of terrestrial organic material (mangrove detritus) and freshwater particulates from the upstream Everglades ecosystem. All the remaining cores from central and western Florida Bay had mean $\delta^{13}\text{C}$ values between $-11.61 \pm 0.72\text{‰}$ and $-9.96 \pm 0.50\text{‰}$, suggesting that seagrass is the dominant organic matter source in the open bay setting. Mean nitrogen isotopic values in central Florida Bay at Bob Allen and Russell Banks were $+4.16 \pm 0.42\text{‰}$ and $+5.24 \pm 0.33\text{‰}$ respectively, whereas the Ninemile Bank core

had a more depleted average $\delta^{15}\text{N}$ value of $+2.22 \pm 0.43\text{‰}$, possibly due to nitrogen inputs originally related to N-fixation in the water column community.

Major events, both anthropogenic and naturally occurring, were evident in the Florida Bay cores, with pronounced shifts in first-order trends and an increase in isotopic variability coincident with the construction of Flagler's Railroad circa 1910, which resulted in decreased exchange between Florida Bay and the Atlantic Ocean. Further changes in the upstream Everglades drainage basin due to canal building circa 1947 also impacted the isotopic and elemental contents of the Florida Bay sedimentary record. In addition, all the major Category 4 and 5 hurricanes of the 20th century to directly impact south Florida were evident in the sedimentary record. Hurricane impacts were most apparent in the sediments of Trout Creek, where Everglades discharge delivered pulses of terrestrial organic material coincident with major storm events.

4.2 INTRODUCTION

Human population growth in coastal areas has precipitated extensive alteration of the quality, quantity, and timing of freshwater runoff into estuaries. In many areas the major water quality change has been an increase in nutrient loading, causing eutrophication of many estuaries and coastal marine systems (Fourqurean et al. 2003). This eutrophication tends to cause shifts in relative dominance between planktonic primary producers and submerged aquatic vegetation, favouring planktonic bloom organisms. Further, marine macrophytes, such as seagrasses, which are prevalent under more oligotrophic conditions, have often been replaced by faster growing, opportunistic

benthic macro- and micro-algae, and also phytoplankton, under conditions of increased anthropogenic nutrient loading (Fourqurean et al. 1993, Duarte 1995). In addition to cultural eutrophication, salinity changes resulting from engineering modifications to freshwater runoff storage and discharge may also influence the distribution and assemblage of submerged aquatic macrophyte communities.

Florida Bay, a 2200 km² shallow subtropical lagoonal estuary, is one such ecosystem which has been affected by human activities over the past century. Canal and trans-Everglades road construction in the early to mid-1900's significantly reduced freshwater flow from the Everglades to Florida Bay via both Shark River and Taylor Sloughs, subsequently leading to increasing periods of hypersalinity in the bay (Smith et al. 1989, Davis and Ogden 1994, Rudnick et al. 1999). Prior to these water management changes however, channel infilling associated with railroad and road construction along the length of the Florida Keys in the early part of the century served to restrict oceanic exchange and circulation between Florida Bay and the Atlantic. These changes in freshwater discharge and circulation are clearly reflected in both fluorescence studies and carbon and oxygen isotopic analyses on coral skeleton cores from several Florida Bay basins (Smith et al. 1989, Swart et al. 1996, 2001).

More recently, over the past two decades, the ecological health of South Florida's coastal ecosystem has increasingly been called into question (McPherson and Halley 1996, Huvane and Cooper 2001, Rudnick et al. 2006). While historically the Florida Bay ecosystem is thought to have been a shallow, optically clear lagoon characterized by low nutrient levels and populated by abundant seagrass communities, in recent years significant declines have been observed in water clarity, hypersaline conditions have

periodically developed in the summer months (Boyer et al. 1999), and widespread die-off events have occurred in benthic seagrass communities (Zieman et al. 1989, Fourqurean et al. 1993), coincident with phytoplankton blooms (Robblee et al. 1991, Butler et al. 1995, Philips and Badylack, 1996). Since 2005, a massive cyanobacterial bloom has persisted in southern Biscayne Bay and Northeastern Florida Bay, yet the causes of the bloom remain uncertain (Rudnick et al. 2006). Although there has been growing concern that these biotic shifts are related to anthropogenic changes in Everglades flow and increasing nutrient inputs from the Florida Keys and the Gulf of Mexico, it is also questioned whether the changes are a consequence of natural phenomena, such as climatic fluctuation or ecological succession cycles (Lapointe and Clark 1992, McIvor et al. 1994, Lapointe et al. 1994, Swart et al. 1999). In the case of the Biscayne Bay – Florida Bay cyanobacteria bloom, the causal mechanisms may in fact be a combination of both anthropogenic and natural phenomena. The bloom is hypothesized to have been caused by the interaction of anthropogenic disturbance related to road construction along US-1 between Florida City and Key Largo with the particularly active hurricane season of 2005, both serving to deliver a large pulse of bioavailable nitrogen and phosphorus, stimulating algal growth (Rudnick et al. 2006). Throughout the inundation history of Florida Bay, it has represented a complex, dynamic ecosystem subject to temporal and spatial variations in environmental conditions (Brewster-Wingard et al. 1999). Prior to significant human impact on the bay, fluctuations in environmental parameters were controlled by natural forces, including hurricanes, climatic variations, and changing sea level.

The Everglades Forever Act (1994) mandates that the ecosystem be returned to its “natural state”; a clear definition of the “natural state” of the Florida Bay ecosystem is thus pivotal to the implementation of restoration efforts. Paleoecological and paleoceanographic reconstructions have become increasingly important to these management decisions in the absence of long term monitoring data. Long term proxy records of environmental change, for example those found in coral skeletons (Smith et al. 1989, Swart et al. 1996, Swart et al. 1999) and those in sedimentary records (Halley and Roullet 1999, Brewster-Wingard and Ishman 1999, Brewster-Wingard et al. 2001, Huvane and Cooper 2001, Cronin et al. 2001, Xu et al. 2006, Xu et al. 2007), provide a baseline understanding of how the South Florida system has changed through time over the last 100 to 4000 years. Despite the growing body of paleoecological data, there remains a large degree of uncertainty about the ecosystem history of Florida Bay (Cronin et al. 2001). This study applies $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values with carbon, nitrogen, and phosphorus elemental compositions of bulk sedimentary organic matter as geochemical tracers in the sediment record over the last 150-200 years in an effort to examine recent environmental changes in Florida Bay, and to gain understanding of the system pre-dating anthropogenic influences. Previous work employing these geochemical proxies, such as Orem et al. (1999) and Nelson et al. (2002), have been limited to a few select locations within Florida Bay and in the mangrove estuaries of the southwestern Everglades, and were completed at a lower sampling resolution than work presented here.

4.3 METHODS

4.3.1 Setting

Florida Bay is a shallow, lagoonal estuary located between the southern tip of the Florida Peninsula and the Florida Keys. The bay has a surface area of approximately 2,200 km² and a mean depth of less than 2 meters (Fourqurean and Robbins 1999, Orem et al. 1999). Sediments have been accumulating in Florida Bay for more than 4000 years over a gradually sloping Pleistocene limestone surface that is 1-4 m below present sea level (Scholl 1964). Basal sediments comprising brackish and freshwater peats and marls similar to those presently accumulating in the Everglades represent the freshwater environment predating marine transgression into the bay (Davies and Cohen 1989). Overlying these freshwater peats are marine carbonate sediments; intercalated silt and clay sized carbonate particles layered with shelly debris horizons. These marine sediments form a network of subtidal mudbanks and mangrove islands that partition the bay into more than 30 small basins, serving to restrict water mixing, and attenuating both tidal amplitude and current. To the west, Florida Bay gradually merges with the Gulf of Mexico; to the east and south the bay is bounded by the Florida Keys, which restrict exchange with the Atlantic Ocean to narrow channels between the islands.

4.3.2 Sample Collection

Sediment cores were collected from four banks in Florida Bay representing the transition from the mangrove ecotone in NE Florida Bay (Trout Creek) through the banks of the middle bay (Russell Key and Bob Allen Bank), out to the western boundary of the bay

(Ninemile Bank) in the summer of 2002 (Figure 4.1; Table 4.1). Piston coring was completed using a pontoon boat mounted tripod, acrylic core barrels (14 cm diameter), a PVC piston with two o-rings and an eyebolt for steel cable attachment to the tripod, and iron handles for gripping the core barrel. The core barrels were pressed down into the soft sediment using the barrel mounted handles, while the piston remained stationary at the sediment surface. Cores were pressed to bedrock where possible and then retrieved by lifting with the handles as the piston stayed fixed in place within the barrel to maintain vacuum. Core bottoms were capped before piston removal and intact cores were transported to the Key Largo Multi-Agency Science Center, Everglades National Park, where they were sectioned into 2-cm intervals. Samples of wet sediment (6cc) were taken from each 2-cm increment for geochemical and stable isotopic analyses which were refrigerated until drying in the laboratory at 70°C. Samples were then powdered and homogenized using a ceramic mortar and pestle.

4.3.3 Geochemical Analyses

Sediment bulk density, % total inorganic carbon (TIC), and % total organic carbon (TOC) were analyzed using standard drying/weight loss upon ignition methods. Sediment organic C and N content were analyzed using a CHN analyzer (Fisons NA1500, Florida International University Seagrass Ecosystems Laboratory), and P content was determined by a dry-oxidation, acid hydrolysis extraction followed by colorimetric analysis of phosphate concentration of the extract (Fourqurean et al. 1992b). Bulk sediment organic matter $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were analyzed using a Thermo Scientific Delta C continuous flow mass spectrometer coupled to a Carlo Erba elemental analyzer

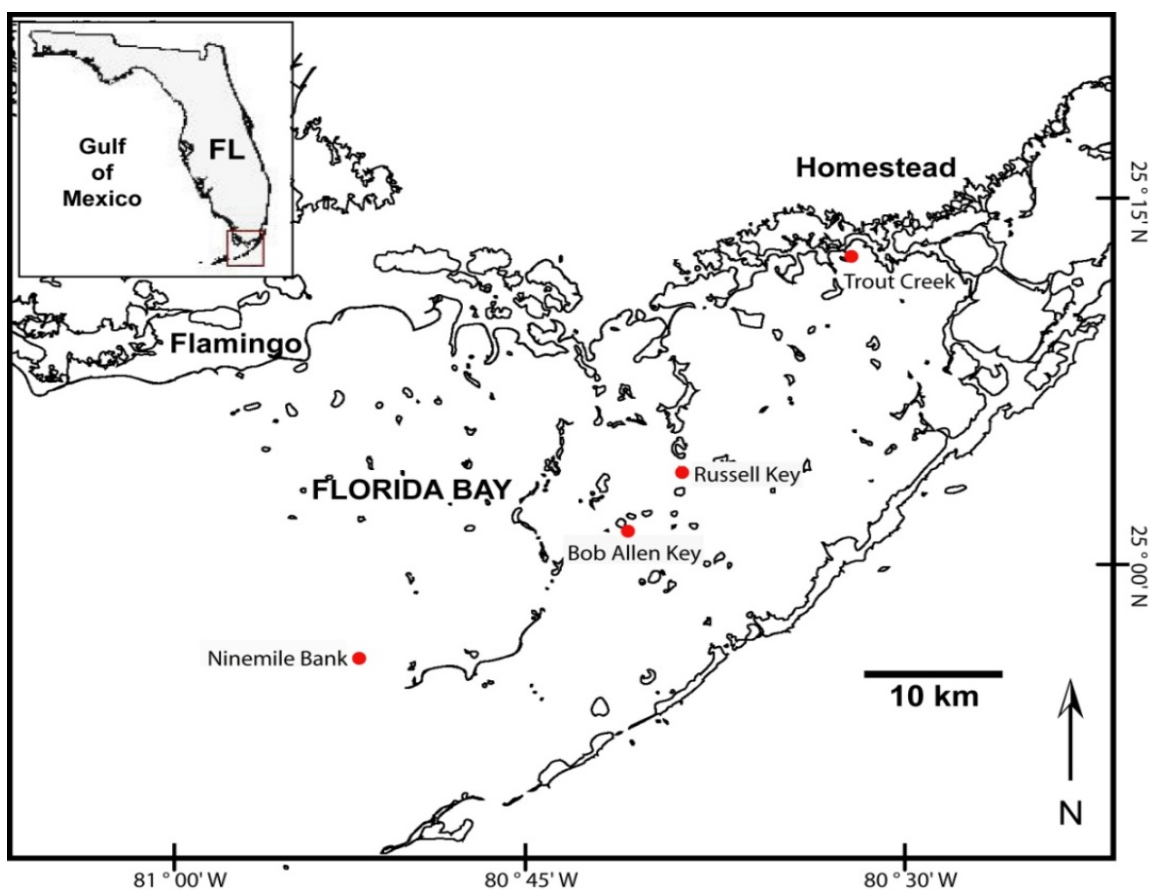


Figure 4.1 Map of Florida Bay, showing core collection sites at Ninemile Bank, Bob Allen Key, Russell Bank, and Trout Creek.

Table 4.1 Florida Bay core locations, calculated average sedimentation rate, core length recovered, and depth with age constraints by ^{210}Pb chronology.

Site	Location		Sedimentation Rate cm/yr	Core length (cm)	Depth of ^{210}Pb chronology (cm)
	N	W			
Trout Creek	25° 12.632'	80° 31.955'	0.6	96	92
Russell Bank	25° 03.871'	80° 37.501'	1.1	166	166
Bob Allen Bank	25° 01.731'	80° 40.795'	0.4	194	66
Ninemile Bank	24° 57.186'	80° 53.545'	0.5	222	98

(EA-IRMS). The EA was used to combust sediment organic material and to reduce the formed gases to N_2 and CO_2 , which were then measured for isotopic ratio in a continuous flow mode. Samples were analyzed for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ before and after acidification to

remove carbonates; $\delta^{15}\text{N}$ was measured on unaltered powdered sediment, $\delta^{13}\text{C}$ was measured on powdered subsamples after acidification with liquid 1N HCl.

Approximately 100 mg of powdered sample were acidified with 20 ml HCl. After 12 hours, acid was decanted and then replaced, and this process was repeated until there was no further effervescence apparent. Samples were then rinsed to neutral pH with deionized water, dried, and analyzed for $\delta^{13}\text{C}$. All values are reported using standard delta (δ) notation relative the international standards of atmospheric N (AIR, N_2) and Vienna Pee Dee Belemnite (V-PDB) for C:

$$\delta = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000 \quad (\text{Eq. 4.1})$$

Where R is the isotopic ratio, i.e. $^{15}\text{N}/^{14}\text{N}$ or $^{13}\text{C}/^{12}\text{C}$ in either sample or standard.

Analytical reproducibility of the reported δ values, based on sample replicates (analyzed every tenth sample) and internal lab standards (also inserted after every block of 10 samples), was better than $\pm 0.2\text{‰}$ for $\delta^{15}\text{N}$ and $\pm 0.08\text{‰}$ for $\delta^{13}\text{C}$.

4.3.4 Age Dating of Sediment Cores

Duplicate cores from each of the sampling sites were dated using ^{210}Pb activity by USGS St. Petersburg, FL using methods described by Holmes et al. (2001) with modifications described by Xu et al. (2007). Samples were dried at 60°C for 48 hours to determine water content and were then ground with mortar and pestle to a fine powder. Five gram subsamples of material were taken for alpha ^{210}Pb analyses. The ^{210}Pb activity was calculated by measuring the alpha activity of the granddaughter isotope, ^{210}Po , assuming secular equilibrium between the two. A leaching process was used followed by autoplating onto silver planchets for alpha counting according to the procedures of Flynn

(1968). Overall counting uncertainties were $\pm 5\%$, determined by triplicate analyses of a subset of samples (Xu et al. 2007). Calculation of sedimentation rates at each site from ^{210}Pb data used the constant rate of supply (CRS) model, which assumes that the flux of ^{210}Pb is constant through time without regard for variability in sediment flux (Holmes et al. 2001, Xu et al. 2007), see Table 4.1. Individual sedimentation rates were generated by applying a best-fit curve to the count data using an unweighted Marquardt-Levenberg parameter optimization method (Press et al. 1989). The advantage of this procedure is that all data points, including negative values resulting from counting errors, are utilized in the calculation of sediment accumulation rate (Holmes et al. 2001). Further, this method corrects for the propagation of ‘old age’ error, inherent in other best-fit interpolations (Holmes et al. 2001). The estimated age resolution for the core chronologies presented here was ± 2 years (Xu et al. 2007). Independent measurements of background ^{226}Ra from sediments in accreting banks in a previous study demonstrated coherent, decreasing linear relationship with depth (r-squared values of 0.6-0.9; Holmes et al. 2001). Subtracting background radium values from ^{210}Pb totals in the 2001 study demonstrated that Florida Bay sediments are in adequate disequilibrium for calculating accurate geochronology (Holmes et al. 2001).

4.3.5 Statistical Analyses

Data were analyzed using a variety of parametric and non-parametric methods. Due to problems with normality and equal variance among cores data sets, the Kruskal-Wallis One-Way Analysis of Variance on Ranks was used to compare geochemical parameters between the four core locations and Dunn’s test was used for post hoc pair-

wise comparisons. Student's t-tests were used to compare paired data sets (i.e. Pre- and post-1910 datasets of each parameter at each specific site) of normally distributed variables, whereas the Mann Whitney Rank Sum Test was used where parametric tests were not appropriate.

4.4 RESULTS

The down-core variations of sedimentary organic $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values for all four cores, together with bulk density, and carbon, nitrogen, and phosphorus elemental ratios, are presented in Figures 4.2-5. In terms of sediment characteristics, all four cores are composed of fine grained carbonate mud interspersed with winnowed shelly debris layers and all cores contained scattered seagrass fragments. X-ray analyses demonstrated no evidence of significant bioturbation or disruption of layering, however the ^{210}Pb chronology in the Bob Allen Bank core showed that the surface sediments at this site date to 1987, suggesting that sediment re-suspension and transport are factors influencing unsheltered mud banks in the central bay. The remaining cores were collected from the accreting leeward bank sides relative to prevailing current directions and show no evidence of scouring.

Table 4.2 $\delta^{13}\text{C}$ (‰), $\delta^{15}\text{N}$ (‰) (Mean \pm SD)

Site	Mean $\delta^{13}\text{C}$ (‰)	Mean $\delta^{15}\text{N}$ (‰)
Trout Creek	-19.64 ± 0.62	5.65 ± 0.59
Russell Bank	-11.34 ± 0.65	5.24 ± 0.33
Bob Allen Bank	-9.96 ± 0.50	4.16 ± 0.42
Ninemile Bank	-11.61 ± 0.72	2.22 ± 0.43

4.4.1 Trout Creek Sediment Geochemistry

The Trout Creek core represents the northeastern end member of the Florida Bay transect, recovered near the mangrove fringe at the mouth of Trout Creek. This area is influenced by one of four creeks draining Taylor Slough in the Southeastern Everglades. This core has the most depleted carbon isotopic signatures (Figure 4.2), ranging between -21.42 and -18.42‰ with an average value of -19.64 ± 0.62 ‰ (Table 4.2). Conversely, the $\delta^{15}\text{N}$ values of the OM in the Trout Creek core were the most enriched of all the cores

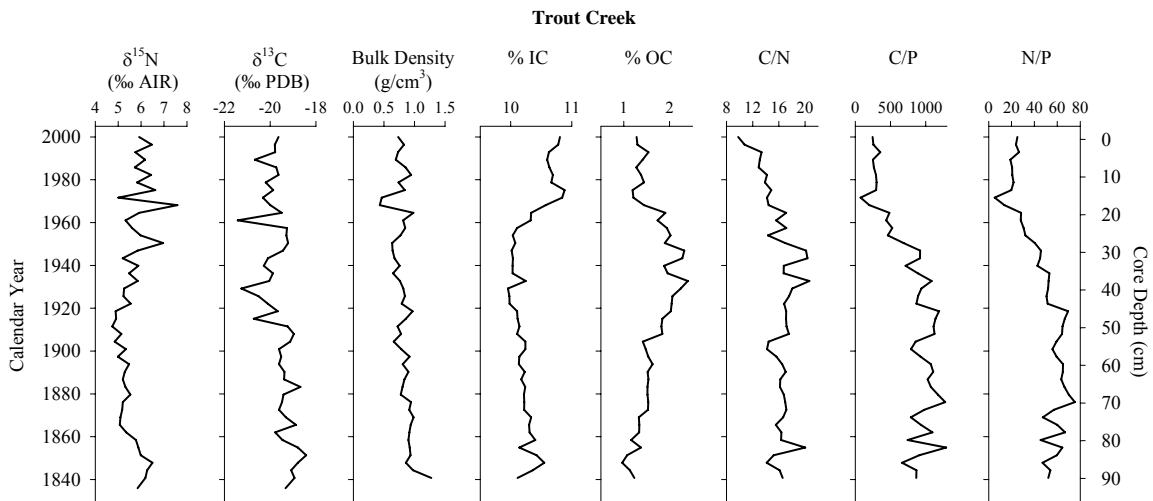


Figure 4.2 Geochemical dataset from the upper 92 cm of a core collected from the mouth of Trout Creek, Northeastern Florida Bay. Carbon and nitrogen stable isotopic data, bulk density, inorganic and organic carbon weight percent, and molar atomic ratios are shown

analyzed, ranging from +4.74 to +7.58‰ with an average value of $+5.65 \pm 0.59$ ‰.

In the lower portion of the core, 1838-1910, all geochemical parameters remain fairly constant, showing no first order trends. Post-1910, however, there was a marked increase in variability, particularly in the carbon and nitrogen isotopic values. Where $\delta^{13}\text{C}$ had shown very little change over time in the lower portion of the core, the upper section is characterized by several negative carbon excursions of up to 2‰ and a slight depletion trend is evident over time. Nitrogen isotopic values after 1910 show a first

order enrichment trend of 1.7‰ with wide fluctuations of up to 2.5‰. Similar pre- and post-1910 trends are also evident in elemental ratios of preserved sedimentary organic matter. Before 1910, molar C/N, C/P, and N/P ratios were all relatively stable, averaging 16.3 ± 1.3 , 980 ± 170 , and 60.1 ± 7.8 respectively. Post 1910 all three parameters show marked declines overtime. C/N decreases to 9.7 while C/P decreases from >1000 to just 245 and N/P decreases from 65 to 25.

4.4.2 Russell Bank Sediment Geochemistry

The Russell Bank core (Figure 4.3) demonstrated more enriched $\delta^{13}\text{C}$ values than Trout Creek, ranging from -12.71 to -10.50‰ with an average value of -11.34 ± 0.56 ‰ (Table 4.2). Nitrogen isotopic values were not significantly different from those in Trout Creek sediments, with an average value of $+5.24 \pm 0.33$ ‰ and ranging between +4.38 and +5.93‰.

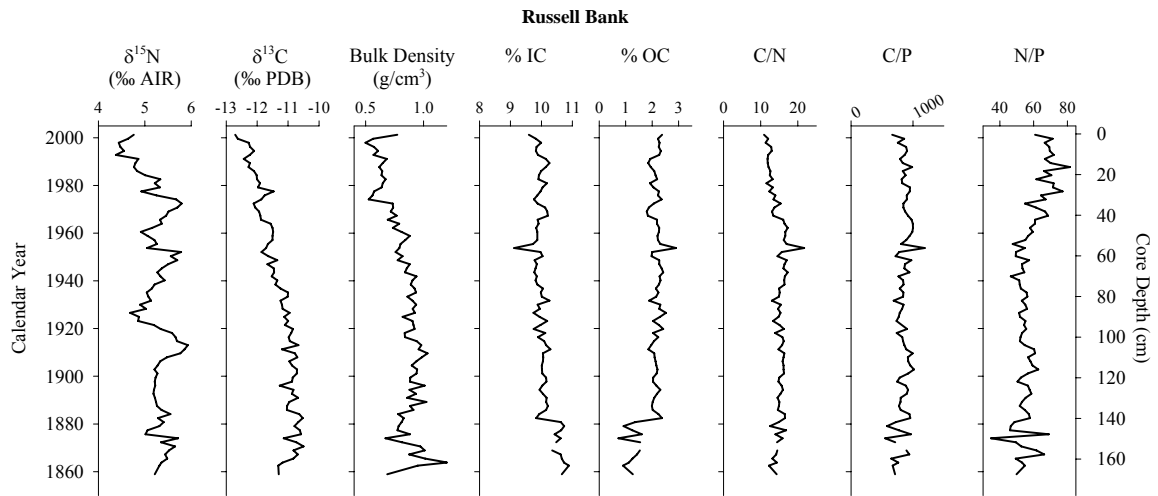


Figure 4.3 Geochemical dataset from a 166 cm long core collected at Russell Bank, Central Florida Bay. Carbon and nitrogen isotopic data, bulk density, inorganic and organic carbon weight percent, and molar atomic ratios are shown.

As observed in the Trout Creek core, carbon and nitrogen isotopic signatures were

consistent in the lower portion of the core. Since 1910, however, $\delta^{13}\text{C}$ became more depleted steadily from -10.8‰ to -12.8‰, while $\delta^{15}\text{N}$ transitioned to a period of high variability, exhibiting a first order depletion trend affecting a 1‰ change with several superimposed second order oscillations. Between 1910 and 1928, $\delta^{15}\text{N}$ values decreased from +5.93 to +4.68‰, then grew more enriched until 1952 (+5.78‰). A second depletion cycle reached a minimum in 1960 (+4.92‰) before increasing to +4.79‰ in 1972. From 1972 to 2002 $\delta^{15}\text{N}$ signatures decreased to an overall minimum of +4.44‰. This final 30 year depletion trend is coincident with a significant increase in molar N/P ratios. This change is largely driven by increasing sediment %N (Figure 4.6). C/N ratios exhibit a slight decreasing trend at this time, but both C/N and C/P remain relatively constant over the full length of the core chronology with means of 14.72 ± 1.64 and 845 ± 98 , respectively.

4.4.3 Bob Allen Bank Sediment Geochemistry

The historical profile of nutrient and isotopic parameters in the Bob Allen Bank (Figure 4.4) sediment column shows trends similar to those observed at Russell Bank, as would be expected of two closely spaced locations in similar mid-bay environments. However, the Bob Allen sediment record has far lower variability, particularly in the organic matter isotopic record, which may be attributable to scouring and reworking of the surface sediments over time, serving to mix sediment packages, averaging out variations. Lower sedimentation rates at Bob Allen Bank, in conjunction with the two centimeter sampling resolution utilized for analyses may also contribute to dampening of potential variability in the sedimentary record by averaging longer time slices in each

individual sample, removing higher frequency variations. As in both Trout Creek and Russell Bank sediment chronology, the lower portion of the Bob Allen Bank core exhibits relative stability in both isotopic and elemental composition, whereas post-1910 sediments record pronounced first order trends and increases in variability. The $\delta^{13}\text{C}$ values show the same 2‰ up-core depletion trend between 1910 and the present as shown at Russell Bank, however Bob Allen Bank sediments are 1-1.5‰ enriched in ^{13}C relative to Russell Bank over the entire sediment history.

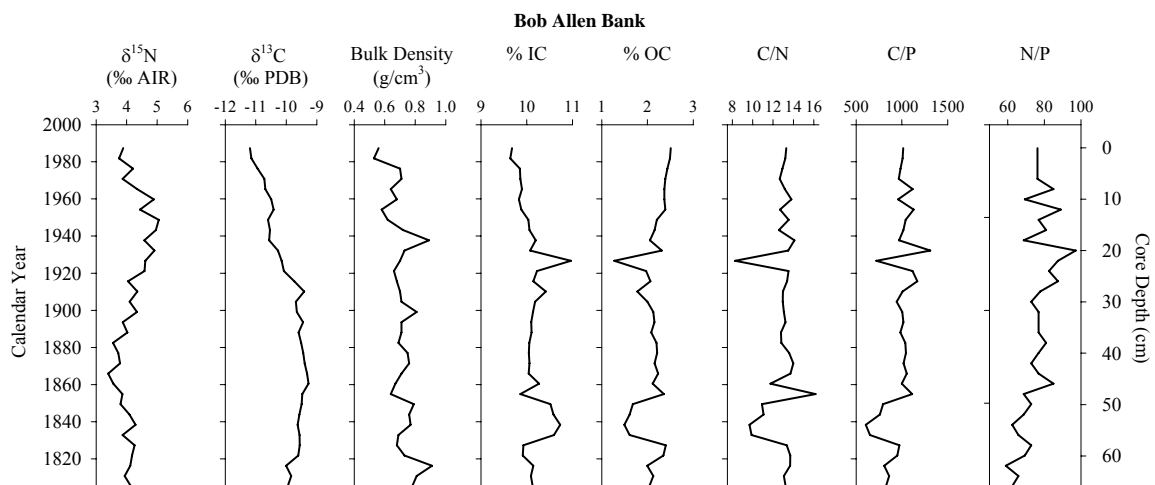


Figure 4.4 Geochemical dataset from the upper 66 cm of a core collected from Bob Allen Bank, Central Florida Bay. Carbon and nitrogen isotopic data, bulk density, inorganic and organic carbon weight percent, and molar atomic ratios are shown.

Values range between -11.19 and -9.27‰ with an average value of $-9.97 \pm 0.56\text{‰}$. The nitrogen isotopic record exhibits similar second order oscillations over time as in Russell Bank post-1910 sediments, however no first order trend is evident, and on the whole, Bob Allen Bank $\delta^{15}\text{N}$ values are more depleted, ranging from +3.39-+5.05‰ with a mean value of $+4.16 \pm 0.42\text{‰}$. Although N/P ratios exhibit increased variability in the upper portion of the core, elemental ratios are consistent with Russell Bank trends also, exhibiting fairly stable values over the entire chronology.

4.4.4 Ninemile Bank Sediment Geochemistry

The Ninemile Bank core (Figure 4.5) represents the western boundary end member of the Florida Bay coring transect, and has been influenced by its proximity to the Gulf of Mexico (GOM) over time. GOM inputs are most obvious in phosphorus content, which has historically been up to three times the concentrations observed in sediments from other areas in Florida Bay (Figure 4.6). Higher P-levels significantly alter C/P and N/P ratios, which were much lower at Ninemile Bank than at the other coring locations,

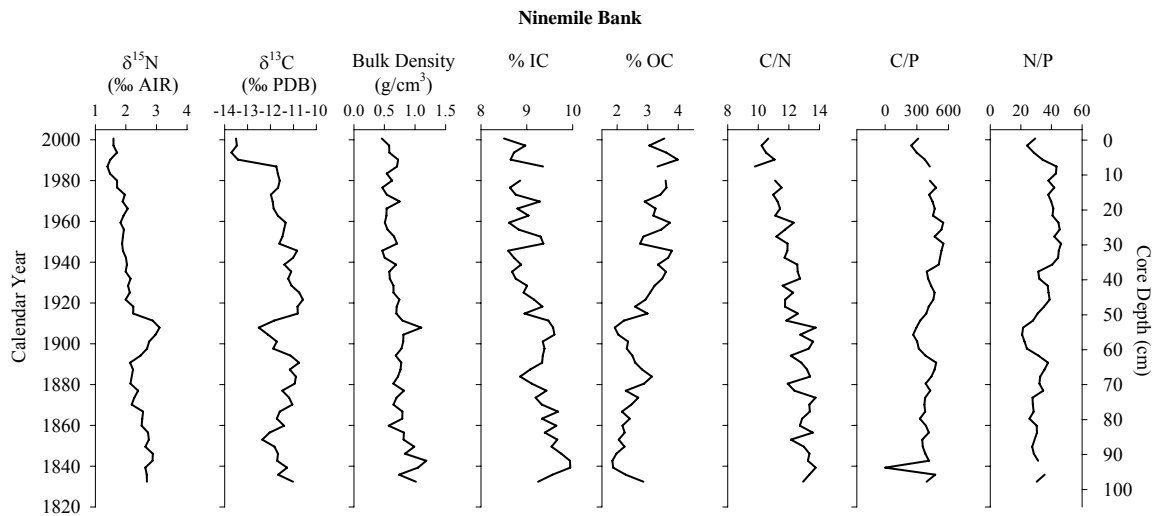


Figure 4.5 Geochemical dataset from the upper 66 cm of a core collected from Ninemile Bank, Western Florida Bay. Carbon and nitrogen isotopic data, bulk density, inorganic and organic carbon weight percent, and molar atomic ratios are shown.

averaging 410.39 ± 73.99 and 34.0 ± 6.9 respectively. Nitrogen isotopic compositions are also significantly different from those preserved in the other cores, exhibiting much more depleted values. The most enriched $\delta^{15}\text{N}$ value, $+3.10\text{‰}$, representing a significant enrichment event coincident with the 1910 inflection point evident bay-wide, is still depleted relative to the lowest $\delta^{15}\text{N}$ value found elsewhere (Bob Allen Bank; $+3.39\text{‰}$). At Ninemile Bank, sedimentary $\delta^{15}\text{N}$ values show a progressive depletion trend throughout the 150 years illustrated here. In contrast to the nitrogen isotope record, $\delta^{13}\text{C}$

values are relatively constant in the lower portion of the core, varying between -11 and -12‰. More depleted values (-12.5‰) correspond to the positive $\delta^{15}\text{N}$ excursion at the turn of the century and are immediately followed by a 2‰ enrichment to -10.5‰ near 1920. Between 1920 and 1980, carbon values show a gradual first order depletion trend of 1‰. A second -2‰ $\delta^{13}\text{C}$ excursion is evident in the most recent 10 years of sedimentary history, with recent values between -13.4 and -13.7‰. Neither C/P nor N/P ratios change significantly up-core, although both ratios decrease synchronously with the 1910 isotopic excursion. C/P values fall from 480 to 295 while N/P ratios decrease from 37 to 20, before recovering to average values, 410.39 ± 73.99 and 34.0 ± 6.91 , respectively. C/N ratios, however, display a progressive depletion trend after 1910, coincident with increasing % organic carbon content. In fact, the Ninemile Bank sediments post-1910 have organic carbon concentrations 1% higher than all other sediments sampled, increasing to 3.5% in the upper core, whereas sediments from the other sites vary between 1.0 and 2.5%. Decreasing C/N ratios while organic carbon content increases demonstrates that nitrogen concentrations have increased at a higher rate than organic carbon burial.

4.4.5 Organic carbon, total nitrogen, and total phosphorus content

Synchronous changes over time in sediment nutrient concentrations may mask variability in nutrient delivery to the Florida Bay ecosystem in the sediment record when only elemental ratios are considered. Concentrations of organic carbon (OC), total nitrogen (TN), and total phosphorus (TP) (all expressed as % dry weight; these data are presented in terms of mass accumulation rate in appendices 3-7) from all coring sites are shown in

Figure 4.6. Concentrations of OC (Figure 4.6a) ranged from less than 1% to greater than 4%. The overall highest concentrations of OC were observed in the Ninemile Bank core, while the lowest OC burial occurred in Trout Creek sediments. Russell Bank and Bob Allen Bank sediments exhibited intermediary OC content of similar magnitude. In fact, while Ninemile Bank and Trout Creek average OC abundances were significantly different from both each other and the paired mid-bay sites, Bob Allen Bank and Russell Bank showed no significant difference in concentration (Table 4.3). In terms of variability over time, the inflection point noted in isotopic values and in most elemental ratios at 1910 (Figures 4.2-5) is clearly reflected in organic carbon delivery and and preservation. Ninemile Bank displayed a 2% increase in organic carbon content, and an apparent increase in variability at that time. An additional inflection point can be seen in 1947, most clearly defined in the Ninemile Bank and Trout Creek sediment records (Figure 4.6). Trout Creek sediments reflect a 1% increase in organic carbon between 1910 and 1940 and then a decrease over the remainder of the sediment chronology. Bob Allen Bank and Russell Bank also display the 1910 shift, however increases in both cores are on the order of only 0.5%.

Total nitrogen concentrations in the sediment records also showed significant variation between coring sites (Table 4.3), ranging from 0.05% to greater than 0.4%, but general trends broadly parallel those seen in OC. Ninemile Bank exhibited the highest TN content, and concentrations followed a similar pattern to that of OC, with a large positive shift and greater variability evident in post 1910 sediments. Russell Bank and Bob Allen Bank had both lower TN concentrations and lower variability than Ninemile

Bank, but also show a change in trend at 1910. Nitrogen content was lowest in Trout Creek sediments and showed an increasing trend over the full core chronology.

The extreme phosphorus limitation so often documented (Fourqurean et al. 1992, 1993, Boyer et al. 1999, Rudnick et al. 1999) for NE Florida Bay is reflected in sediment total phosphorus concentrations throughout the last 150 years of sedimentation. TP concentrations vary in the mid-bay and NE ecotone sites (Bob Allen Bank, Russell Bank, and Trout Creek) between 0.003% and 0.040%, approaching detection limits for analyses. Sediments at Ninemile Bank clearly reflect Gulf of Mexico inputs, with up to

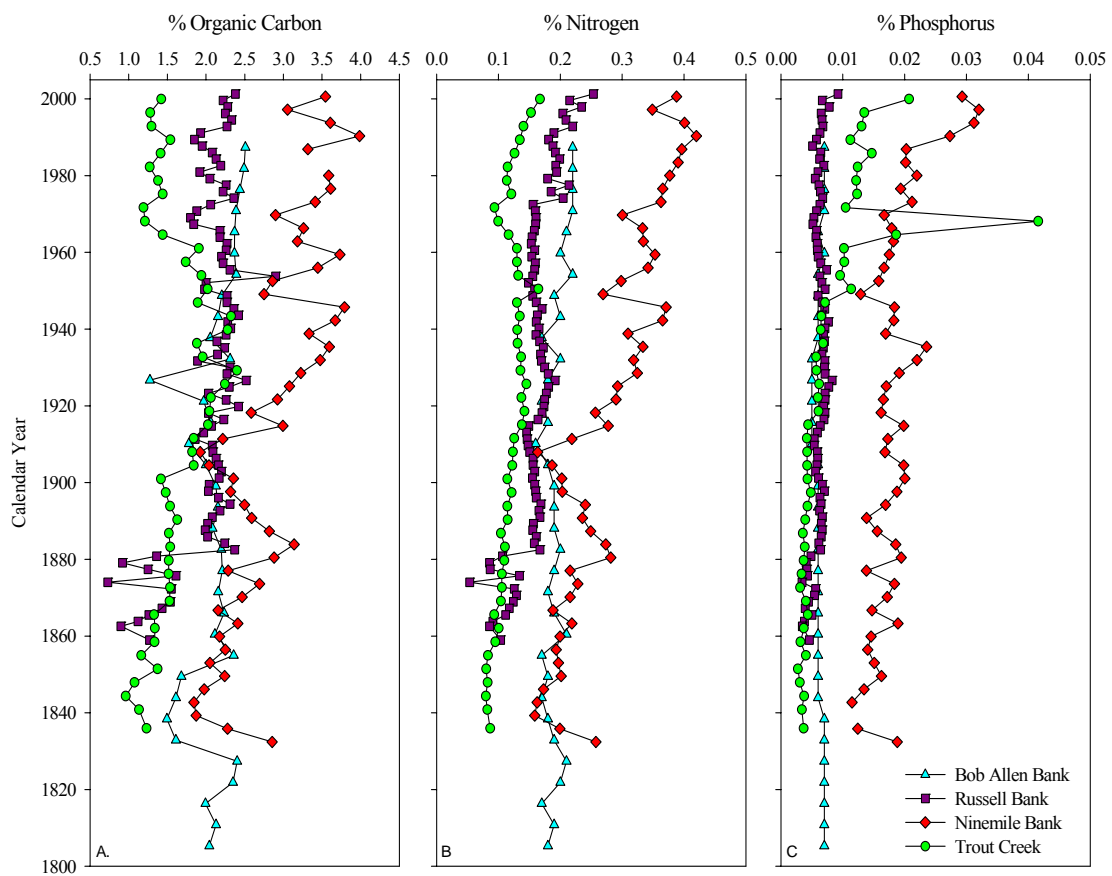


Figure 4.6 Sediment elemental composition data over time at four sites in Florida Bay expressed in weight %. A) Organic carbon B) Nitrogen C) Phosphorus.

Table 4.3 Percent elemental compositions and calculated molar ratios for each core (Mean \pm SD).

Site	% OC	%N	%P	Molar C:N	Molar C:P	Molar N:P
Trout Creek	1.60 \pm 0.36	0.12 \pm 0.02	0.008 \pm 0.007	15.89 \pm 2.4	755.57 \pm 345.4	46.04 \pm 18.5
Russell Bank	2.06 \pm 0.45	0.16 \pm 0.03	0.006 \pm 0.001	14.72 \pm 1.6	845.80 \pm 98.2	57.95 \pm 8.0
Bob Allen Bank	2.11 \pm 0.30	0.19 \pm 0.02	0.006 \pm 0.0007	12.83 \pm 1.4	969.89 \pm 146.8	75.66 \pm 8.3
Ninemile Bank	2.84 \pm 0.60	0.28 \pm 0.08	0.018 \pm 0.004	12.26 \pm 1.0	410.39 \pm 74.0	34.04 \pm 6.9

three times higher %TP. In terms of temporal trends, both Trout Creek and Ninemile Bank sedimentary TP displayed a distinct increasing trend after 1947, resulting in doubled TP concentrations in both cores.

4.4.6 Carbon and nitrogen isotopic signatures

Significant spatial variability was evident in both C and N isotopic data (Figure 4.7). Trout Creek sedimentary $\delta^{13}\text{C}$ data very clearly distinguished the mangrove ecotone from open water Florida Bay banks, with more depleted values relative to all other cores (Table 4.2). Bob Allen Bank sediments exhibited the most enriched $\delta^{13}\text{C}$ signatures, with Russell Bank and Ninemile Bank approximately 1‰ enriched. In terms of $\delta^{13}\text{C}$, both Trout Creek and Bob Allen Bank were significantly different from Ninemile and Russell Banks, however, the latter two sites show no statistical difference in $\delta^{13}\text{C}$ values. Ninemile Bank was the most isotopically distinct site in terms of $\delta^{15}\text{N}$, with significantly depleted values (Table 4.2). Bob Allen Bank preserved more enriched $\delta^{15}\text{N}$ values at an average of 4.16‰. Trout Creek and Russell Bank were both significantly enriched relative to both Bob Allen Bank and Ninemile Bank, however there was no significant difference between the two.

The distinct pattern inflection at 1910 evident in sediment nutrient content is also shown by the sediment organic matter isotopic values (Figure 4.7; open symbols indicate

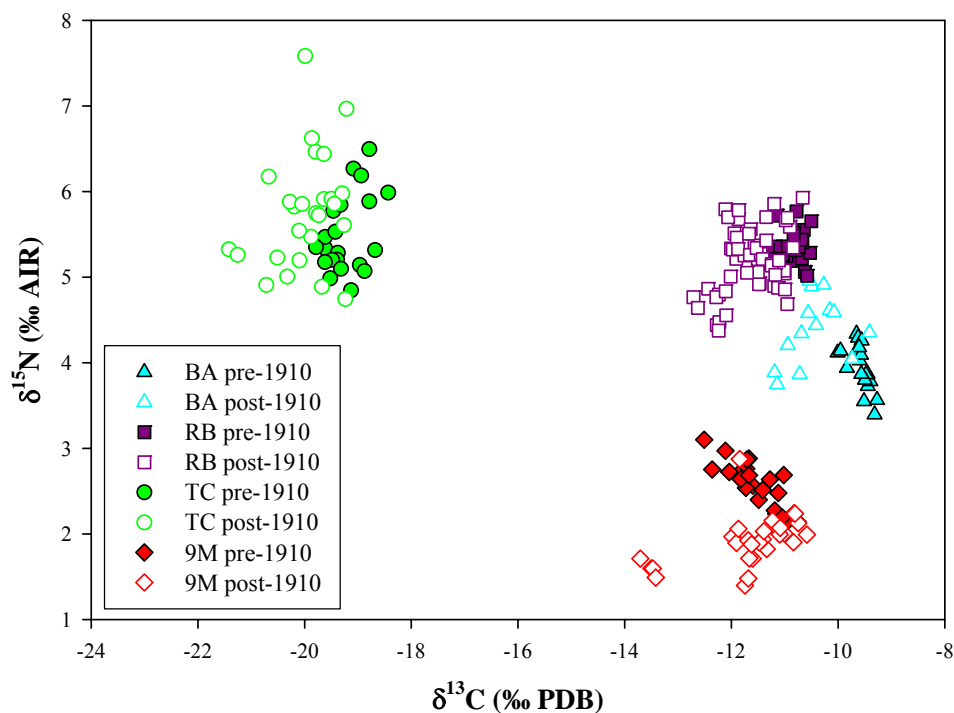


Figure 4.7 Carbon and nitrogen isotopic data from four Florida Bay cores: Bob Allen Bank (BA), Russell Bank (RB), Trout Creek (TC), and Ninemile Bank (9M). Closed symbols denote data from core stratigraphy between 1850 and 1910; open symbols denote data from 1910 to 2002.

Table 4.4 Sediment geochemical parameter means \pm st. dev. comparing pre- and post-1910 data sets

Core	Interval	$\delta^{13}\text{C}$ (‰ V-PDB)	$\delta^{15}\text{N}$ (‰ AIR)	C:N	N:P	C:P	n
TC	pre-1910	-19.22 ± 0.37	$+5.50 \pm 0.46$	16.33 ± 1.29	60.07 ± 7.76	984.17 ± 171.30	21
	post-1910	-19.98 ± 0.58	$+5.77 \pm 0.67$	15.53 ± 2.92	34.71 ± 16.77	570.94 ± 341.6	26
	<i>p-value</i>	<0.001	0.113	0.556	<0.001	<0.001	
RB	pre-1910	-10.85 ± 0.22	$+5.34 \pm 0.18$	15.10 ± 1.19	54.78 ± 6.75	827.74 ± 125.70	30
	post-1910	-11.62 ± 0.49	$+5.19 \pm 0.38$	14.52 ± 1.82	59.68 ± 8.21	855.67 ± 78.95	54
	<i>p-value</i>	<0.001	0.055	0.295	0.007	0.491	
BA	pre-1910	-9.58 ± 0.19	$+3.94 \pm 0.27$	12.77 ± 1.54	71.822 ± 6.77	918.03 ± 141.90	19
	post-1910	-10.46 ± 0.48	$+4.43 \pm 0.42$	12.90 ± 1.35	80.513 ± 7.66	1035.6 ± 129.00	15
	<i>p-value</i>	<0.001	<0.001	0.84	0.001	0.018	
9M	pre-1910	-11.53 ± 0.47	$+2.56 \pm 0.28$	13.07 ± 0.11	29.31 ± 4.57	381.33 ± 57.28	23
	post-1910	-11.69 ± 0.87	$+1.91 \pm 0.30$	11.54 ± 0.76	37.82 ± 6.12	434.98 ± 78.50	27
	<i>p-value</i>	0.653	<0.001	<0.001	<0.001	0.011	

sediment data post- 1910; Table 4.4). Carbon isotope values at mid-bay and mangrove ecotone sites (Bob Allen Bank, Russell Bank, and Trout Creek) all show a significant negative carbon isotopic shift in post 1910 sedimentary records. Greater variability in $\delta^{13}\text{C}$ values was also evident at these sites after 1910. Mean $\delta^{15}\text{N}$ values showed no change between pre- and post-1910 datasets at Trout Creek and Russell Bank; however, variability in the data did increase after 1910 at both sites. At both Bob Allen and Ninemile Banks, statistically significant shifts in $\delta^{15}\text{N}$ values were apparent in pre- versus post-1910 sediments. At Bob Allen Bank, N-isotopic values grew more enriched, while at Ninemile Bank isotopic composition became progressively more depleted after 1910. $\delta^{13}\text{C}$ values was also evident at these sites after 1910. Mean $\delta^{15}\text{N}$ values showed no change between pre- and post-1910 datasets at Trout Creek and Russell Bank; however, variability in the data did increase after 1910 at both sites. At both Bob Allen and Ninemile Banks, statistically significant shifts in $\delta^{15}\text{N}$ values were apparent in pre- versus post-1910 sediments. At Bob Allen Bank, N-isotopic values grew more enriched, while at Ninemile Bank isotopic composition became progressively more depleted after 1910.

4.5 DISCUSSION

4.5.1 Isotopic and elemental source characterization

Tracing carbon flow in an estuarine ecosystem by stable C isotope techniques is possible because of large differences between the $\delta^{13}\text{C}$ values of terrestrial and marine primary producers. In the case of Florida Bay, these differences are among mangrove, seagrass, and both macro- and microalgal inputs. Atmospheric CO_2 , the carbon source

for plants, has a $\delta^{13}\text{C}$ value of approximately -8.0‰ (Francey and Allison 1996), yet terrestrial plants utilizing the Calvin Cycle (C_3 photosynthetic pathway) as a carbon fixation mechanism have an average $\delta^{13}\text{C}$ of -27‰. This fractionation results from isotopic selectivity of RUBISCO (ribulose-1,5-biphosphate carboxylase) preferentially utilizing ^{12}C . Carbon fixation in aquatic plants such as seagrasses, however, may be significantly influenced by diffusive boundary limitations which decrease isotopic discrimination and cause much smaller isotopic depletions relative to environmental CO_2 isotopic compositions (Andrews and Abel 1981, Benedict et al. 1980). Nitrogen isotopic values in estuarine organic matter reflect more complex dynamics, influenced by the interplay of nutrient source variations both in isotopic value and N-species (nitrate versus ammonium), by chemical fractionation related to remineralization, N-fixation, and denitrification processes operating on source pools, and by fractionations associated with nutrient uptake and incorporation into biomass.

Representative isotopic compositions and sparse molar C:N data for various potential organic matter sources to Florida Bay sediments are given in Table 4.4. The strong disparity between terrestrial and aquatic plant materials in terms of carbon isotopic composition is readily apparent, with seagrasses and mangrove organics representing enriched versus depleted signatures, while aquatic macroalgae and particulate organic matter fall as intermediates. The three open water Florida Bay cores (Russell Bank, Bob Allen Bank, and Ninemile Bank) all display carbon isotopic signatures characteristic of seagrass organic material through the entire sediment record (Figure 4.7; Kieckbusch et al. 2004, Fourqurean et al. 2005, Behringer and Butler 2006). Bulk sediment C:N ratios in these three cores however vary between 10 and 14, representing lower values than

Table 4.5 Representative isotopic and elemental compositions of terrestrial versus marine organic matter sources to Florida Bay.

	Genera	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)	Molar C:N	reference
Terrestrial					
Floc		2.4 ± 1.1	-29.0 ± 9.1	11.3	Williams and Trexler 2006
Periphyton		2.6 ± 1.0 3.2 to 4.7	-28.3 ± 2.1 -28 to -22	13.6	Williams and Trexler 2006 Wozniak et al. 2008
Sawgrass	<i>Cladium</i>	1.0 to 2.7	-25 to -22		Wozniak et al. 2008
Mangrove	<i>Rhizophora</i> <i>Rhizophora</i> <i>Rhizophora</i> <i>Rhizophora</i> <i>Rhizophora</i> <i>Rhizophora</i>	0.1 ± 1.0 5.5 ± 0.5 8.0 6.0	-26.2 ± 0.59 -28.7 ± 1.4 -26.7 ± 0.3 -26 to -30 -27 -27	100	Kieckbusch et al. 2004 Fourqurean and Schrlau 2003 Lin et al. 1990 Fleming et al. 1990 Zieman et al. 1984 Zieman et al. 1984
Marine					
POM*		0.5 to 4.0 1.8 4.9 ± 0.23	-14 to -20 -18.0 -18.4 ± 0.06		Mumford 1999 Behringer and Butler 2006 Kieckbusch et al. 2004
Macroalgae	<i>Penicillus</i> <i>Caulerpa</i> <i>Halimeda</i> <i>Laurencia</i> <i>Laurencia</i> mixed ave. mixed ave.	1.7 ± 1.9 2.3 ± 0.82 1.0 ± 0.76 1.4 2.3 ± 0.1 	-18.3 ± 0.39 -15.8 ± 3.57 -18.9 ± 3.23 -13.8 -16.2 ± 3.4 -13 -22		Kieckbusch et al. 2004 Kieckbusch et al. 2004 Kieckbusch et al. 2004 Kieckbusch et al. 2004 Behringer and Butler 2006 Zieman et al. 1984 Zieman et al. 1984
Seagrass	<i>Thalassia</i> <i>Thalassia</i> <i>Thalassia</i> <i>Thalassia</i> <i>Syringodium</i> <i>Syringodium</i> <i>Halodule</i>	1.4 ± 0.24 6.0 ± 0.3 2.8 ± 0.6 -5 to +9 0.7 2.0 -2 to +4	-11.5 ± 2.81 -10.7 ± 0.2 -6.5 ± 0.7 -15 to -7 -10.7 -8 to -4 -15 to -9	17 22.6 18 to 22 18 to 22	Kieckbusch et al. 2004 Fourqurean and Schrlau 2003 Behringer and Butler 2006 Fourqurean et al. 2005 Kieckbusch et al. 2004 Fourqurean <i>unpub. data</i> Fourqurean <i>unpub. data</i>
Epiphytes		4.1 ± 0.8 2.6 ± 0.16 2.7-8.3	-12.3 ± 1.6 -16.7 ± 0.52 -24		Behringer and Butler 2006 Kieckbusch et al. 2004 Mumford et al. 1999 Zieman et al. 1984

* Particulate Organic Matter

those measured in modern Florida Bay seagrass tissues (20-25; Fourqurean et al. 1992a, b, Fourqurean et al. 2005). Preferential mineralization of N relative to C during early

diagenesis has been documented in a number of sedimentary environments (Herczeg et al. 2001, Meyers 1997) resulting in increasing C:N as diagenesis proceeds. The apparent overall secular decrease in the C:N ratio of Florida Bay sedimentary organic matter is thus not attributable to organic degradation of seagrass material. One possible mechanism involves bacterial utilization of external nitrogen source inputs, which serves to increase N content of bulk sedimentary organics as bacterially-mediated carbon remineralization occurs, resulting in decreasing C:N (Rice and Hanson 1984, Lamb et al. 2006, Lamb et al. 2007). Alternatively, preservation of an organic mixture including planktonic, epiphytic, or benthic microalgae could contribute a component with much lower C:N (Redfield C:N for planktonic algae varies from 4-6; bacterial C:N is generally <10; Redfield 1934, Meyers 1994, Tyson 1995).

Particulate organic matter C-isotopic compositions measured Bay-wide vary between -20 and -15‰ (Mumford 1999, Evans et al. 2006). In many cases more labile organic components are isotopically enriched, so that degradation results in isotopic depletion of residual material (Macko et al. 1993, DeLang et al. 1994, Prahl et al. 1997, Ogrinc et al. 2005); however, isotopic enrichment with degradation of highly labile particulate material has also been documented (Valiela et al. 1985, Guo et al. 2004). Such processes could lead to $\delta^{13}\text{C}$ values considered characteristic of seagrasses in organic material of algal origin. The $\delta^{13}\text{C}$ of bulk sedimentary organic material at open bay core locations reflects both seagrass and microalgal inputs over the last 150 years. Xu et al. (2007) demonstrated similar results in organic biomarker records from the open bay core locations. Seagrasses and microalgal biomarkers dominated in Russell Bank, Bob Allen Bank, and Ninemile Bank cores, showing changes similar to those in the

isotope values in the frequency and magnitude of concentration oscillations after the turn of the century (Xu et al. 2007). The depleted $\delta^{13}\text{C}$ values of Trout Creek sediments suggest a stronger influence of terrigenous organic matter (Lin et al. 1991); which is also in agreement with organic biomarker evidence of mangrove OM inputs to the sediments at Trout Creek. Xu et al. (2006) showed 7000 ng/g sediment of the mangrove biomarker, taraxerol, in surficial sediments from Trout Creek while there was less than 300 ng/g sediment in western Florida Bay. This dominance of mangrove organic biomarkers was also observed through the entirety of the Trout Creek core, corroborating the isotopic evidence of terrigenous organic material (Xu et al. 2007). Mangrove material was expected to be the main OM source in Trout Creek sediments, because of the close proximity of Taylor Slough freshwater discharge and the southern Everglades mangrove ecotonal fringe. Mixing between marine and terrestrial organic matter inputs is necessary to explain $\delta^{13}\text{C}$ values falling between those typical of mangroves (-26‰) and local seagrasses (-12 to -7‰). Again however, like the open Florida Bay core sites, C:N values at Trout Creek have been much lower over the entire sediment history than those expected of either seagrass (>20) or mangrove (generally >50; Ruttenberg and Goni 1997, Yamamuro 2000)) organic material. Although Xu et al. (2006, 2007) found significant concentrations of taraxerol, and much lower concentrations of algal markers, C:N values as low as 8 imply that there is either a significant algal input of organic matter or a significant bacterial component and high level of carbon remineralization altering C:N ratios preserved in the sediment at Trout Creek. In a similarly distributed core study, Orem et al. (1999) found fine fraction sediment organic C:N ratios in the same range found here, which they attributed to the greater N content of organic matter derived from

algae rather than either terrestrial plants or seagrasses.

Interpretation of nitrogen isotopic values is more complex than carbon due to the web of geochemical N-cycling processes and different isotopic fractionations among those processes, competing fractionation associated with species-specific uptake, and differences in diagenetic alteration of various organic nitrogenous substrates. Many studies invoke the nitrogen isotopic composition of sedimentary organic matter as a direct record of surface water nutrient utilization and paleoproductivity, explaining organic matter $\delta^{15}\text{N}$ values as a product of Rayleigh fractionation kinetics (Calvert et al. 1992, Francois et al. 1992, Altabet and Francois 1994, Minoura et al. 1997). Yet, nutrient utilization and paleoproductivity have not successfully explained the sedimentary record in lake sediments (Teranes and Bernasconi 2000), perhaps because phosphorus, rather than nitrogen, is the primary limiting nutrient in lacustrine settings. When only a small portion of ambient nitrogen is consumed, the nitrogen isotopic composition of the dissolved inorganic nitrogen pool is never significantly altered.

Relative nutrient limitations in Florida Bay are primary factors in understanding the nitrogen isotope record preserved at various locations in the Bay. Analogous to many lacustrine settings, and like many shallow carbonate environments, it is commonly held that South Florida coastal waters are generally phosphorus limited (Lapointe 1987, Lapointe and O'Connell 1989, Short et al. 1990, Fourqurean et al. 1992a, b, Fourqurean et al. 1993, Frankovich and Fourqurean 1997, Brand 2002). Calcium carbonate chemically scavenges phosphate from seawater (DeKanel and Morse 1978), thus phosphorus concentrations in Florida Bay, particularly in the northeastern zone, are commonly very low, often approaching the limits of analytical detection (Boyer et al.

1997). However, there is a significant gradient from east to west in phosphorus availability, as Gulf of Mexico inputs, in addition to abundant phosphorite deposits along the west coast of Florida, serve as a source of much higher phosphorus concentrations in the western boundary zone (Boyer et al. 1997, 1999, Brand 2002). An opposing gradient exists in available nitrogen, with high dissolved inorganic N availability in the northeast decreasing to limiting levels in the west (Boyer et al. 1997, Brand 2002). Most of the N is delivered in freshwater discharge from the Everglades-agricultural system via Taylor Slough and the South-Dade Water Conveyance System canals. While phosphorus may also be present in the upland zone of the agricultural drainage, carbonate geochemical scavenging and efficient vegetation P-assimilation result in downstream discharge of nitrogen-rich, phosphorus-poor runoff (Brand 2002). Thus in the nitrogen replete, phosphorus limited zone of NE Florida Bay, organic nitrogen isotopic values are likely to reflect nutrient sources, whereas in the N-limited W Florida Bay, $\delta^{15}\text{N}$ values are more likely to reflect not only initial source isotopic composition, but may be complicated by nutrient utilization and microbial recycling of nutrient pools. Interestingly however, the Trout Creek core, collected from the high-nitrogen NE Florida Bay zone, exhibits the most variable and enriched sediment organic $\delta^{15}\text{N}$ compositions of all the cores (Figure 4.7). These enriched values (up to +8‰) may reflect the influence of denitrification in the anoxic sediments of the adjacent mangrove ecotone leading to inputs of nitrogen with more enriched isotopic compositions in residual nutrients, or upstream use of organic waste fertilizer in the Everglades agricultural zone resulting in enriched nutrient sources discharging through Taylor Slough. The two most positive N-isotopic excursions, representing over 2‰ fluctuations, are coincident with peak % phosphorus

concentrations preserved in the sediments. Large enrichments over mean $\delta^{15}\text{N}$ may be the expression of nutrient utilization and residual enrichment during bloom events triggered by pulses of high phosphorus availability in the zone of severe P-limitation.

The remaining three core locations, distributed along the east to west gradient in N-availability, show a progressive down-gradient depletion in terms of nitrogen isotopic composition, with the most depleted signals in the western bay zone (exhibiting the lowest ambient N concentrations in the modern environment). The transition evident in mean sedimentary organic matter isotopic composition is consistent with the modern distribution of $\delta^{15}\text{N}$ values measured in leaves from the dominant seagrass of the region, *Thalassia testudinum*. Fourqurean et al. (2005) showed a similar spatial pattern, with more enriched $\delta^{15}\text{N}$ values in NE Florida Bay and adjacent to the mangrove ecotone, transitioning to lower values along the E-W axis of Florida Bay. It would seem then that the nitrogen isotopic values preserved in the sediment organic material also reflect the dominance of seagrass inputs. More depleted $\delta^{15}\text{N}$ values in the western zone may be tied to the prevalence of cyanobacteria associated with Shark River discharge and along much of the SW coastline (Brand 2002). Drifter trajectories show significant transport paths moving Shark River flow and SW coastal nutrient sources along the western boundary of Florida Bay, passing through Florida Keys channels around Long Key (Lee et al. 2002). These flow-paths cross directly over the Ninemile Bank core collection site, and it can be assumed that this has been the case through recent history. Further, Evans et al. (2006) showed depleted $\delta^{15}\text{N}$ values coincident with a bloom of such cyanobacteria, indicating N-fixation as a possible nitrogen source in the N-limited zone. Higher inputs of either cyanobacterial organic material, or seagrass material grown with recycled N

initially fixed by cyanobacteria, could account for the lower nitrogen isotopic values and increases in %N content preserved throughout the section of Ninemile Bank sediment history presented here.

4.5.2 Anthropogenic influences on Florida Bay over time

The most significant geochemical changes evident in the last 150 years of sediment history recorded in the cores presented here are the concurrent shifts in the complete suite of geochemical parameters evident just after the turn of the century. Prior to 1910 nearly all parameters exhibited relatively constant values with no obvious first order trends. Following 1910, however, bay-wide sedimentary records of elemental and isotopic compositions transition to a phase of increased variability, and long term trends develop over the remainder of the century. This shift, present regardless of sedimentation rate and organic material sources, is too coincidental to reflect a diagenetic pattern down-core. Carbon isotopic compositions of all open-bay cores (Russell Bank, Bob Allen Bank, and Ninemile Bank) all show a trend of progressive depletion trend after 1910 (Figures 4.3-5). While this isotopic trend could reflect gradual changes in organic matter source, favouring more isotopically depleted marine algal inputs, this hypothesis is not supported by organic biomarker indicators of algal input measured on the same cores (Xu et al. 2007). Seagrass biomarkers showed dramatic increases in abundance over this time period in all cores, whereas algal biomarkers increased significantly only after 1980 in all cores except Russell Bank, where algal markers were abundant between 1880 and 1970 (Xu et al. 2007). Gradual depletion in $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC), reconstructed based on both mollusk shell (Halley and Roulier 1999) and coral skeleton

(Swart et al. 1996) carbon isotopic values, follows an abrupt shift at between 1905 and 1912. The change just after the turn of the century was attributed to the construction of Flagler's Railroad along the Florida Keys and concurrent infilling of several Keys channels (Swart et al. 1996, Brewster Wingard et al. 2001). Filling the passes decreased circulation and exchange with the Atlantic Ocean, serving to increase the residence time of water masses in Florida Bay basins, and allowing more of the isotopically depleted oxidative decomposition products to be retained within the water column (Swart et al. 1996, Halley and Roulier 1999). Not only was this isotopically depleted inorganic carbon incorporated into carbonates over time, but also in organic material subsequently preserved in the sediments.

Similar changes have been documented in many studies, whose results are further confirmed here. Foraminiferal and molluscan assemblage data from cores collected at Bob Allen Bank and Russell Bank show long term increases in salinity, switching to a highly fluctuating salinity regime after 1900 (Brewster-Wingard and Ishman 1999). These faunal indicators seem to vary on a 20-year cycle as recorded at Russell Bank, whereas Bob Allen Bank showed only a few fluctuations of longer duration. Similar patterns are shown by the nitrogen isotopic compositions of the Bob Allen Bank and Russell Bank cores presented here. It may be that the lower sedimentation rate and higher propensity for scouring and resuspension of sediments at Bob Allen Bank dampens the record of second order oscillations. However it may also be a factor that Russell Bank is located in a more interior, isolated basin of Florida Bay, while Porpoise Lake, of which Bob Allen Bank is a northern boundary, is connected to Lignumvitae Basin to the SW and Cotton Key Basin to the SE, both of which have some level of

connectivity directly to the Atlantic Ocean, thus may benefit from higher levels of flushing and exchange then would a more isolated interior basin. In more isolated basins of the bay, climatic fluctuations controlling evaporation and freshwater flow would likely have generated higher variability in water column parameters.

While there is a strong argument for the importance of the hydrologic circulation changes precipitated by railroad construction in the early 1900's supported by the pervasive shift in all geochemical parameters measured, first order depletion trends of 1.5 to 2 ‰ seen in all the sediment organic matter $\delta^{13}\text{C}$ records presented here are consistent with depletion trends in coral and sclerosponge skeleton $\delta^{13}\text{C}$ records (Figure 4.8) (Swart et al. 1996, Swart et al. 2002).

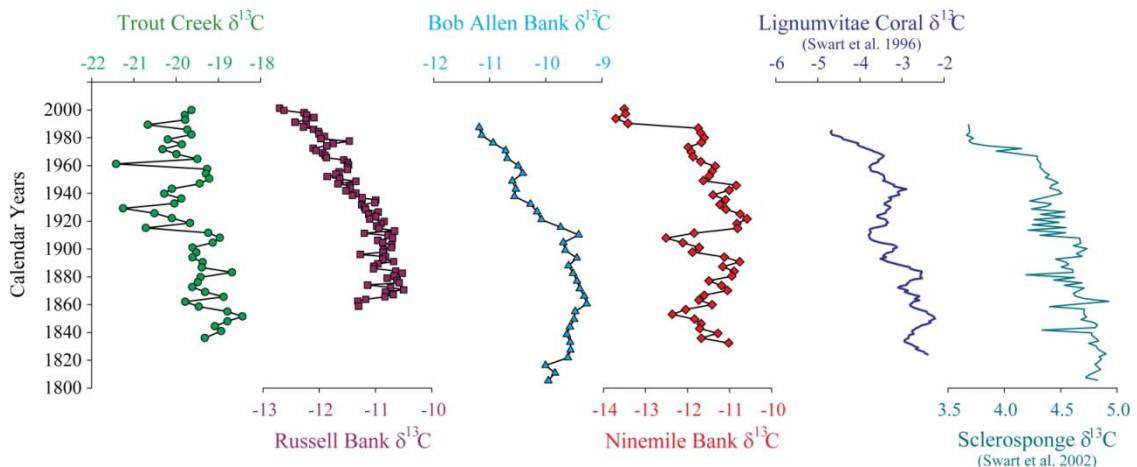


Figure 4.8 Carbon isotopic data from all Florida Bay cores plotted with two $\delta^{13}\text{C}$ datasets from Swart et al., a coral record (Swart et al. 1996) and a sclerosponge record (Swart et al. 2002). A gradual 1.5-2‰ depletion can be seen in all these regional records which is consistent with the Suess Effect.

The long-term depletion in OM and skeletal records reflect the progressive depletion in atmospheric $\delta^{13}\text{C}$ resulting from the burning of fossil fuels since industrialization, a change conventionally known as the Suess Effect (Revelle and Suess 1957, Cialis et al. 1995, Swart et al. 1996, Swart et al. 2002, Francey et al. 2002, Anderson et al. 2005). In

addition to the major shift in geochemical trends coincident with altered circulation patterns and the advent of the Suess Effect atmospheric changes, a depletion trend is evident in $\delta^{15}\text{N}$ after 1945 at the interior Florida Bay sites, Bob Allen Bank and Russell Bank. Also, a shift toward increasing variability in isotopic values is apparent after 1935 in the Trout Creek record, coincident with trends toward lower values in all elemental ratios (C:N, N:P, and C:P). The timing of these changes reflects the onset of large scale water management altering freshwater delivery to Florida Bay from the Everglades.

By 1930, the backbone of major canals diverting freshwater east to the Atlantic rather than south through the Everglades to Florida Bay was in place, and Tamiami Trail construction, bisecting the Everglades, leaving only culvert flow connecting the northern and southern parts of the drainage basin, was complete (Light and Dineen 1994). Later, drainage of the Everglades was greatly accelerated after 1947 with the development of the South and Central Florida Flood Control Project, an initiative which lowered the water table and reduced the flow of freshwater to Florida Bay, increasing its overall salinity and shifting Florida bay from a brackish to often hyper-saline ecosystem (Light and Dineen 1994, Smith et al. 1989, McIvor et al. 1994, Brand 2002). These profound changes in freshwater delivery to the Florida Bay system are clearly evident in the Trout Creek core, collected near the outflow of Taylor Slough (Figure 4.2). Here, significant decreases in elemental ratios suggest lower allocthonous mangrove inputs, resulting in less terrestrial organic carbon preservation. While there is an increase in variability of concentrations of organic biomarkers indicative of mangrove inputs during this time interval, it coincides with overall trends of increasing concentration in the Trout Creek core (Xu et al. 2007). Lower organic carbon storage may result from decreasing

freshwater flow, nutrient flux, and autochthonous productivity. Alternatively, decreasing organic carbon contents may be the result of increased organic decomposition related to longer residence times as a consequence of lower freshwater flushing.

The impact of changes in water management in the Everglades has been demonstrated in a number of proxy studies in the past. Both the studies of coral fluorescence by Smith et al. (1989) and in mollusk shells by Brewster-Wingard et al. (1999) showed an amplification of the frequency and magnitude of salinity fluctuations after 1940, attributable to changes in water management practices following completion of the South Florida Canal System that served to reduce and disrupt the natural freshwater flow into Florida Bay. Further, ostracod (Cronin et al. 2001) and diatom (Huvane and Cooper 2001) assemblages also exhibit synchronous and marked shifts at this time. These studies postulate increases in benthic seagrass community dominance after 1950; it seems reasonable then, that decreases in freshwater delivery and ensuing increases in Florida Bay salinity actually drove the proliferation of marine seagrass benthic communities. Restoration of historic flow patterns may therefore degrade these marine communities.

4.5.3 Hurricane history

In addition to the pronounced geochemical traces left by changes in anthropogenic influence over the Everglades watershed and Florida Bay in the 20th century, naturally occurring climatic catastrophes have also left geochemical fingerprints recorded in the sedimentary history of Florida Bay. Several major hurricanes have impacted South Florida during the past century. Most notable on the list include the un-

named September hurricane of 1919 (Category 4 on the Saffir-Simpson Scale), the Labor Day Hurricane of 1935 (Category 5), Hurricane Donna of 1960 (Category 4), and Hurricane Andrew in 1992 (Category 5). Major tropical cyclones cause immediate and longer term environmental changes in the coastal zone due to sediment erosion and deposition, and storm induced bidirectional sediment transport (Tabb and Jones 1962, Wanless et al. 1994). Such sediment disturbance has been identified in cores from several banks in Florida Bay, demonstrated by discontinuities in ^{210}Pb records coincident with storms in 1935, 1948, 1960, and 1992 (Kang and Treyfry 2003, Alvarez-Zarikian et al. 2001).

In addition to sedimentation pulse disturbances, heavy precipitation associated with storm events has also historically been evident in excessive freshwater discharge through the Everglades sloughs (Kang and Treyfry 2003, Donders et al. 2008). These pulses almost certainly carry high levels of mangrove detritus to the adjacent estuarine system, particularly if the storm event is associated with high windfield impacts resulting in defoliation of coastal mangrove forests (Wanless et al. 1994). In a sediment core study from Rookery Bay, one of the estuaries of the SW Florida Shark River Slough drainage, Donders et al. (2008) found a direct correlation between the major South Florida hurricane events and mangrove pollen minima, coincident with disturbance-indicative maxima in ragweed pollen. These results were interpreted to imply high levels of mangrove mortality in storm events, thus precluding pollen production in year(s) following the storms, and invasion of ragweed and low level shrubs in disturbed canopy gap areas (Donders et al. 2008). Indeed, impact analysis studies of Hurricanes Donna (1960) and Andrew (1992) show that the main impact on the natural communities

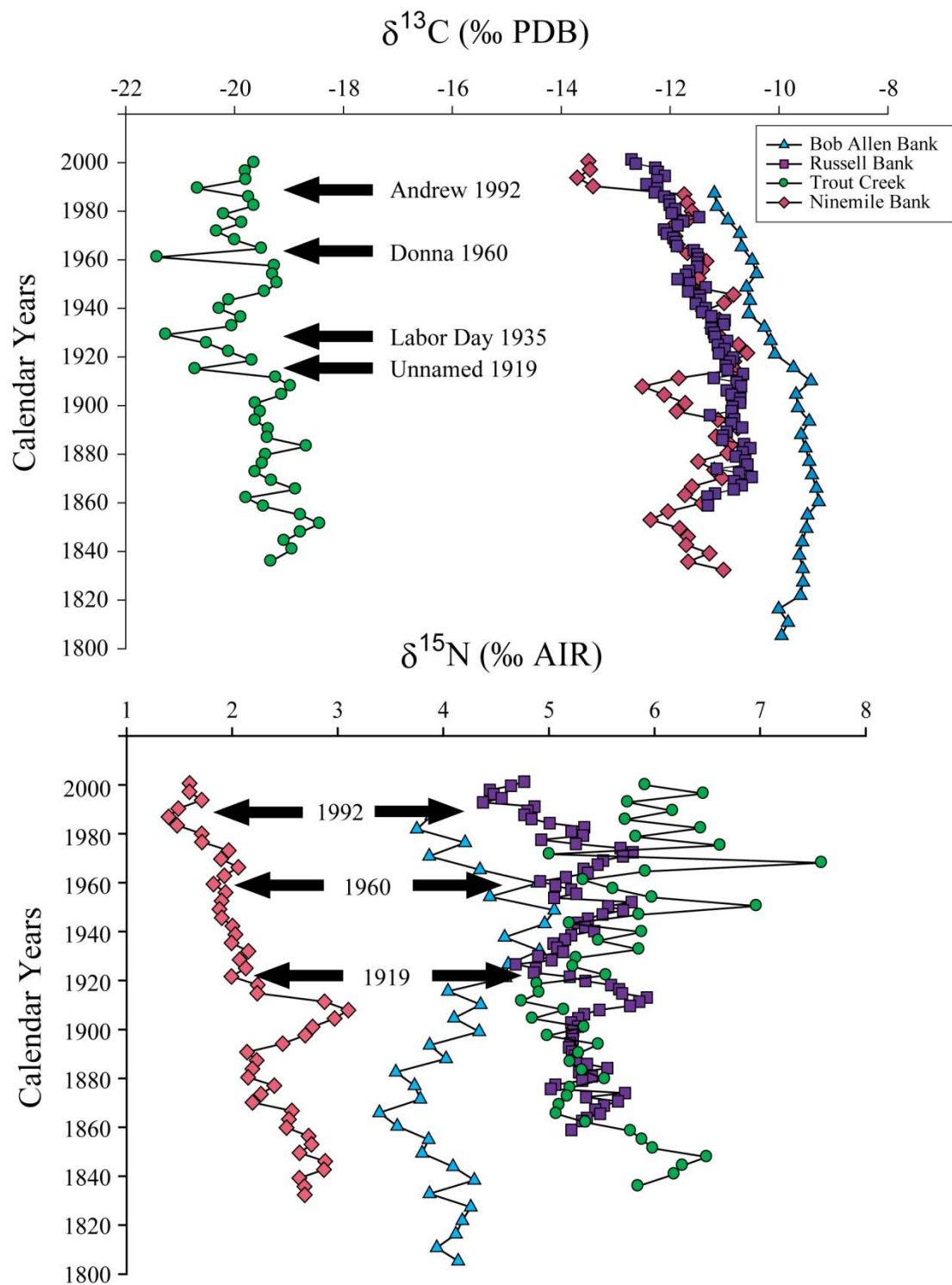


Figure 4.9 Carbon and nitrogen isotope stratigraphy from the four Florida Bay cores highlighting isotopic evidence of hurricane disturbance.

occurred as destruction of interior wetland, rather than coastal erosion (Tabb and Jones 1962, Wanless et al. 1994, Doyle et al. 1995). Both these storm events caused some coastal erosion along Florida's Southern mangrove coastline, however the predominant impact was widespread destruction of mangrove canopy (Wanless et al. 1994). Carbon isotopic values evident in the Trout Creek core seem to support these conclusions. Four distinct negative isotopic excursions of up to 2.5 ‰ are apparent, suggesting large, yet temporally isolated, fluxes of mangrove-derived organic material coincident with documented hurricane events of 1919, 1935, 1960, and 1992 (Figure 4.8). This conclusion is supported by the work of Xu et al. (2007) on the same core, as peaks in the concentration of the mangrove organic biomarker, taraxerol, are evident at levels consistent with inputs related to Hurricanes Andrew and Donna (1992 and 1960). Unfortunately biomarker sampling resolution was not coincident with the earlier isotopic markers of hurricane influence found in the Trout Creek record, and since the duration of the storm fluxes are so temporally isolated, these storms were missed in the taraxerol record.

In the Ninemile Bank core, two negative isotopic excursions of approximately 2‰ can be seen in the $\delta^{13}\text{C}$ record; the most recent appears to begin in the early 1990's coincident with Hurricane Andrew (Figure 4.5). A second period of carbon isotopic depletion is evident at the turn of the century, and persists for over 20 years. This earlier excursion may be related either to "The Great Freeze" of 1899 (Myers et al. 1986), a cold snap that resulted in a massive fall of mangrove foliage, or it may be the isotopic expression of the mangrove clearing for the purpose of building of the Flagler Railway (1907-1912; Wardlaw 2001). While Xu et al. (2007) did find slight increases in taraxerol

fairly consistent in time with the events recorded in the bulk sedimentary isotopic record, the taraxerol concentrations found in the Ninemile Bank core are two orders of magnitude lower than those measured in the Trout Creek core and were interpreted to indicate low mangrove organic inputs in the western bay zone. Increases in C₂₅ HBI (highly branched isoprenoids, an organic biomarker for certain species of marine diatom; Xu et al. 2006, 2007) are also evident in intervals near 1900 and between 1985-1995 (Xu et al. 2007), so the negative carbon isotopic shifts could be related to increased phytoplankton/epiphytic diatom organic material inputs. Sediment elemental compositions in this core also seem to support algal sources, as this interval has lower organic carbon and nitrogen contents, coincident with increased sediment phosphorus. These concentrations could imply phytoplankton blooms as a source of organic material of different carbon isotopic composition, stimulated by increased phosphorus availability. Further, enriched $\delta^{15}\text{N}$ values over the 20 year interval could be indicative of increased surface nitrogen utilization during bloom conditions. In fact, diatom/algal blooms could be stimulated by nutrients released through degradation of mangrove organic matter inputs, thus both could contribute to the depleted $\delta^{13}\text{C}$ values in these intervals. The Ninemile Bank carbon isotopic excursions differ from those preserved in the Trout Creek core in that they are persistent for up to 20 years in the open bay setting, whereas Trout Creek values, proximal to Taylor Slough freshwater discharge from the Everglades, suggest very short duration episodic events. This difference in time-span of preserved inputs is likely a function of residence time in bay versus creek settings. Presumably isotopically depleted carbon released by mangrove decomposition would be continuously recycled in the open bay, whereas freshwater flow in Trout Creek would serve to quickly

flush dissolved components released via mangrove decomposition so preservation of the pulse signal in the sediment would be expected to be more restricted in time.

Interestingly, while all four major hurricanes preserved in the Trout Creek sediment organic isotopic record are not apparent in the isotopic records of the other Florida Bay cores, though three of the four are perhaps recorded in the nitrogen isotopic compositions of the Ninemile and Russell bank cores as subtle negative excursions of less than 1‰ (Figure 4.9). These negative perturbations might be related to nitrogen fixing cyanobacterial populations stimulated by detritus decay release of nutrients following storm events. This contention is supported by correlations with all four storm major events preserved in the organic carbon, nitrogen, and phosphorus content of the sediments (Figure 4.6). In the Ninemile Bank core there are peaks in all three elemental contents apparently coincident with the same 1919, 1935, 1960, and 1992 major storms. At Bob Allen Bank, minor increases in C:N ratios, coincident with decreases in N:P occur in intervals roughly concurrent with the 1960, 1935, and 1919 storms. These ratio changes are driven by small decreases in sediment N-content. Given the evidence in the ^{210}Pb chronology that scouring and sediment transport is a significant influence on Bob Allen Bank, it is likely that sediment resuspension during the hurricane events facilitates oxic degradation of sedimentary organic matter and preferential N-removal. There are also 0.5 ‰ enrichments in $\delta^{15}\text{N}$ preserved in the 1960 and 1935 intervals which may also indicate preferential degradation of nitrogenous compounds during resuspension, as has been shown to occur in many studies of suspended particulate organic matter (Altabet 1988, Saino 1992, Macko et al. 1987, Holmes et al. 1997, Freudenthal et al. 2001). These

results indicate that high magnitude storm events are differentially preserved in geochemical records depending on the individual character of local environments.

4.6 CONCLUSIONS

Changes in sediment geochemical characteristics over time at four coring locations along a central axial transect of Florida Bay provide a record of change over the past 150+ years. Coincident shifts in first order trends and increasing fluctuation levels after 1910 at all sites indicate that bay-wide events and regional changes in the ecosystem have occurred, resulting in variations in organic material inputs and nutrient availability. Changes in sediment organic isotopic composition and elemental abundances exhibit high spatial heterogeneity and are dependent on the physical characteristics of different basins, not unlike the zones of similar influence model currently utilized to describe modern Florida Bay. Changes restricting circulation and altering of freshwater delivery through the Everglades watershed, including the construction of Flagler's Overseas Railroad in the early 1900's, Tamiami Trail in the 1930's, the South Dade Conveyance Canal System circa 1947, and the Water Conservation areas in 1965, have had profound impact on the Florida Bay system, and this is as evident in bulk sedimentary geochemical parameters as it is in very specific faunal assemblage or organic biomarker studies. Certainly, bulk organic material should not be overlooked, because while in some cases further proxies are necessary to clarify complex processes controlling these parameters, there is a wealth of historic information preserved in this material. Carbon isotopic data from all open bay cores seems to indicate predominance of seagrasses in terms of organic inputs to the sediments over the last 150 years. In addition, long term depletions in the $\delta^{13}\text{C}$ of

atmospheric and aqueous CO₂, recognized in inorganic carbon proxies such as coral skeletons and shell material as well as in ice core and tree ring records, can also be observed in long term changes in the carbon isotopic composition of organic material. Gradients in relative nutrient limitation can be seen in preserved organic material isotopic compositions, particularly in sediment organic nitrogen, as this organic material is a product of the ambient conditions under which it was produced.

While the influence of anthropogenic disturbance since the turn of the century is clearly a dominant factor preserved in the recent sedimentary record of Florida Bay, bulk organic geochemistry data also record the occurrence of major hurricane activity, with negative excursions in both carbon and nitrogen isotopic values, confirming documentary evidence of hurricane landfalls of sufficient magnitude to cause significant damage to upstream mangrove wetlands. These impacts may provide a potential tracer for detecting hurricane events prior to historical documentation in high resolution sediment studies.

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CHAPTER 5

CONCLUSIONS AND FUTURE STUDIES

5.1 CONCLUSION

In coastal South Florida, long term management plans for restoration of natural flow conditions through the Everglades increase the importance of understanding potential nutrient impacts of increased freshwater delivery on coastal biogeochemistry. Part of the impetus behind the isotopic studies documented here lay in exploring spatial and temporal variability in planktonic community composition and relationships to nutrient parameters in light of the variability observed over ten years of isotopic monitoring in benthic seagrass communities (Fourqurean et al. 2005) and in consideration of changes in biotic community structure evident over the last three decades, with increased incidence of plankton blooms and declining seagrass densities in many areas (Fourqurean and Robblee 1999). The further objective of this work was to examine the sediment record in Florida Bay to assess the preservation of variability in organic material over a longer time scale. Thus the main goal of this dissertation was to examine components of the isotopic systematics of the South Florida marine system, at a variety of time scales. At the process level, OM stable isotopic values were applied to assess nutrient acquisition mechanisms in a single transient cyanobacterial bloom event. From a longer term seasonal point of view, isotopic values demonstrated a high level of spatial and temporal variability in POM, supporting previous work characterizing the significance of hydrodynamic regime as a control on coastal processes. Increasing the scale further, geochemical data was utilized to assess organic matter source and identify markers of disturbance in the last century. The unifying feature of the isotopic data presented here is the high level of variability exhibited on all time scales.

5.2 ISOTOPIC VARIABILITY IN POM

The isotopic composition of POM in near-shore and estuarine settings provides important information about ambient environmental conditions, biotic community structure, and biogeochemical cycling within the system. This information may be used to infer changes in primary productivity and water quality parameters in increasingly environmentally sensitive coastal settings and in the case of South Florida, could become a valuable tool to evaluate future downstream impacts of modifications to Everglades hydrology.

5.2.1 Nitrogen fixation in transient cyanobacterial blooms

In the present study, OM stable isotopic values were applied to assess nutrient acquisition mechanisms in a transitory cyanobacterial bloom event, demonstrating spatial heterogeneity across a relatively short distance between northeast and western Florida Bay in process-controlled OM isotopic character. In many marine settings, carbon and nitrogen isotopic signatures have been interpreted in terms of surface nutrient utilization and productivity levels (Altabet and Francois 1994, Altabet 1988), yet the isotopic data in the first part of the work presented here demonstrates nitrogen isotopic depletion, rather than enrichment, coincident with a surface plankton bloom. This isotopic depletion has implications regarding the importance of biologically fixed nitrogen as a nutrient source during bloom events, particularly in nitrogen-limited marine environments. While these observations are not revolutionary, N-fixing plankton blooms are of course widespread, geochemical documentation of spatially isolated new nitrogen inputs to the coastal system are relevant in terms of understanding nutrient cycling and delivery in the local

coastal environment. This situation becomes particularly significant when the connection between phosphorus availability and cyanobacterial bloom organisms capable of supporting their own nitrogen demand is considered in terms of changing Everglades hydrology. As has been seen in the persistent Southern Biscayne Bay/Northeastern Florida Bay plankton bloom (2005-present) any change in phosphorus delivery (for example a road construction project and/or a major pulse in hurricane frequency) may upset the ecosystem balance, opening the system to pervasive ecological disturbance (Rudnick et al. 2006). In the coastal Florida carbonate platform environment phosphorus is the limiting nutrient for primary productivity (Fourqurean et al. 1993), however that could change if restoration of Everglades flows served to deliver higher levels of agricultural runoff into the coastal zone. Any perturbation in phosphorus availability could support bloom forming organisms either in zones characterized by high or low nitrogen availability, with species assemblages adapted to appropriate N-acquisition mechanisms.

5.2.2 Spatial and temporal isotopic variability in size-fractionated POM

From a seasonal point of view, POM isotopic values exhibited a high level of spatial and temporal variability, yet this variability was distributed in a pattern supporting previous work characterizing the significance of hydrodynamic regime as a control on coastal nutrient processes and ecology (Boyer et al. 1997). Clearly planktonic communities respond to seasonal changes in environmental parameters, although driving mechanisms vary in space and time. In the case of the South Florida coastal zone, differences in all environmental parameters are dependent on the hydrodynamic regime

of various areas in terms of geomorphological constraints and physical mechanisms of nutrient delivery and transport (Rudnick et al. 1999, Boyer et al. 1997). Geochemical cycles in POM fractions reflect these patterns in hydrodynamic regime, showing seasonal changes controlled by factors specific to localized zones of influence and as a result, exhibit a remarkable level of isotopic heterogeneity. Significant differences were observed between both size classes and sampling locations in terms of isotopic values and seasonal patterns in POM; $\delta^{13}\text{C}$ values varied by up to 22‰ while $\delta^{15}\text{N}$ values showed seasonal changes of up to 7‰. Interestingly, the range in isotopic values observed in POM varying on both spatial and seasonal scales exceeds that exhibited by benthic seagrasses in the region (Fourqurean et al. 2005), suggesting that the variation in POM isotopic composition is not entirely driven by particulate contributions from the benthic community. Furthermore, the seasonal variations in POM isotopic character documented here are of a magnitude equal to the long term changes observed in sedimentary records spanning geologic time scales on the order of millions of years (Haug et al. 2000, Minoura et al. 1997), yet were observed on a single carbonate platform over just two years of seasonal cycling. The result is autochthonous OM that is geochemically variable even over short distances, which has implications to future study attempting to characterize coastal processes without well distributed sampling schemes. As well, the level of spatial and temporal variability of isotopic composition, inconsistency in isotopic values between size classes, and also differences between size fractionated and bulk POM samples have implications for current assumptions regarding the interpretation of bulk filtered POM samples as they are applied to understanding food-web studies, studies of organic matter sources to the coastal zone, and natural tracer

experiments examining anthropogenic influences in the coastal environment. All these studies must take into account spatial and temporal changes in the stable isotopic composition of POM when interpreting relationships and patterns.

5.2.3 Limitations of the POM time-series

Despite the importance of POM in aquatic ecosystems, studies of POM are hindered by several methodological constraints. One of the most important is that POM is highly heterogeneous, consisting of living and dead cells, fecal pellets, marine snow aggregates, organically coated mineral grains, and other materials, each of which may exhibit different spatial and temporal variations depending on source and chemical transformations (Minor and Nallathamby 2004). Separating particulates on the basis of size does not alleviate difficulties inherent in understanding the geochemical character of a variable mixture of particle sources. For example, while the $>150\ \mu\text{m}$ size fractionation can be operationally defined as the “zooplankton” fraction, in fact larval zooplankton can be captured in smaller size classes, which was observed microscopically in the particulate fractions collected. Additionally, separating by particle size also does not allow the separation of living plankton from detritus particles of uniform size. Advances have been made that help alleviate these sample corruptions, particularly for POM in the pico-nanometer range quantified with flow cytometry. Minor and Nallathamby (2004) utilized cell sorting features available on certain flow cytometers in conjunction with isotopic ratio mass spectrometry to obtain more specific isotopic values. Obviously data are limited by the capabilities of available instrumentation. Manual sorting of larger size fractions is one possible solution to the mixed isotopic signal, however would require

much larger sample volumes and a very significant time commitment in order to sort particles into individual samples of sufficient mass for further geochemical analyses.

Further limitations of the dataset are evident from a statistical point of view.

While the sampling design employed provided statistically valid descriptive data illustrating seasonal changes in POM geochemical, this design was less suited to correlation analyses between the isotopic cycles either within or between the size classes, or between the size classes and various environmental parameters potentially affecting them. Correlation requires high frequency sampling and an evenly spaced representation along a given physical or chemical gradient. Cyclic phenomena such as seasonal productivity cycles, nutrient drawdown, and episodic change, either in nutrient delivery or climate patterns, undermine correlations where there are lags in responses (Rolff 2000, Savoye et al. 2003). Improving sampling resolution from quarterly to monthly or even biweekly would increase not only the potential for correlation analyses, but also would of course generate much clearer seasonal patterns, as a single sample collected at 3 month intervals is unlikely to truly represent a seasonal mean in terms of geochemical character. So many variables may influence the composition of POM at any given location, including weather (wind and precipitation), tidal forcing, biological species succession, episodic nutrient delivery, and probably a host of other factors, that it is unrealistic to expect a single sampling interval to represent average conditions. Additional statistical limitation was incurred by logistical constraints on sampling. Available time and infrastructure on site during each sampling interval allowed for the collection of one size-fractionated sample per site. While over 300 samples were collected to build the isotopic time series, lack of replication precluded between site comparisons of individual seasons.

5.3 FLORIDA BAY SEDIMENTARY RECORDS

One of the main objectives of this research was to apply new understanding of modern variability in POM isotopic systematics to increase understanding of the sedimentary record in Florida Bay. While the high level of variability observed in POM isotopic signatures is complicated in terms of direct application to the sediment record, these data do have some significant implications to understanding preserved OM. Isotopic signals suggesting nitrogen fixation in western Florida Bay and the strong connectivity between seasonal patterns in POM isotopic character and hydrodynamic regime convolute conventionally accepted paradigms of sediment record interpretation. Relative $\delta^{15}\text{N}$ enrichment or depletion is not necessarily indicative of surface nitrogen utilization in situations where nitrogen is not the limiting nutrient (Teranes and Bernasconi 2000, Lehmann et al. 2004), nor when changes in nitrogen fixation or denitrification rates exert influence over the isotopic character of nitrogen pools (Haug et al. 2000, Ren et al. 2008). Thus even process-oriented short-term observations of isotopic fractionation or microbial nitrogen cycling shifts are in fact connected to long term sediment records.

Autochthonous OM produced in the various hydrodynamic zones of influence around South Florida exhibits a remarkable level of isotopic heterogeneity. Also, this magnitude of spatial and temporal fluctuation in isotopic composition has been documented, albeit over a smaller range in isotopic values, in seagrasses (Anderson and Fourqurean 2003, Fourqurean et al. 2005), and in marine algae (Lapointe et al. 2004, Lapointe et al. 2005). Recent work has demonstrated linkages between variability in

water column processes, particularly in terms of nitrogen cycling and the isotopic character of POM, with sinking particles and preserved sedimentary organic material (Haug et al. 2000, Teranes and Bernasconi 2000, Ren et al. 2008), thus the high degree of heterogeneity apparent in both planktonic and benthic OM production from the South Florida coastal zone can be expected to control the character of OM preserved in sediments. Indeed, similar to the spatial heterogeneity evident in the modern setting in terms of the isotopic character of OM, cores collected from relatively closely spaced locations in Florida Bay show a high level of discordance in isotopic values, as well as elemental compositions. The $\delta^{13}\text{C}$ values from all the open Florida Bay coring locations indicate the predominance of seagrasses as OM source, however values are slightly depleted, implying mixing with marine planktonic OM sources. The $\delta^{13}\text{C}$ of sediment organic material proximal to the Everglades outflow in northeastern Florida Bay is further depleted, indicating terrestrial OM represents a significant component of perhaps a three-end member mixing model combining seagrass with planktonic OM, in addition to terrestrial inputs. While these source distributions are shown with relative clarity by $\delta^{13}\text{C}$ records, $\delta^{15}\text{N}$ values in bulk sediment OM seemed to reflect some of the processes evident in the modern POM studies. Nitrogen isotopic values in western Florida Bay sediments were depleted relative to all other coring locations, similar to patterns observed in the POM isotopic signal. Organic matter inputs related to the planktonic nitrogen fixation observed in the western zone generated a pervasive signal evident over time in the sedimentary record. The central and northeastern Florida Bay core sedimentary organic nitrogen records demonstrate the importance of hydrodynamic setting in OM geochemical character, with differences in nitrogen isotopic values shown between basins

influenced by varying degrees of hydrologic restriction (i.e. Russell Bank is in a more isolated basin and had more enriched $\delta^{15}\text{N}$ values over the length of the core record examined than in the less isolated Bob Allen Bank core record).

Superimposed on the spatial heterogeneity evident in sediment OM geochemical records are the impacts of major anthropogenic changes to the system in the last century. Coincident shifts in first-order trends and increasing fluctuation levels after 1910 at all sites indicate bay-wide events and regional changes in the ecosystem occurred coincident with railroad construction in the Florida Keys, resulting in variations in organic material inputs and nutrient availability. Further, perhaps more subtle, yet equally pervasive, are shifts concurrent with the large changes in Everglades drainage systems circa 1950. The expression of such changes in terms of sediment organic isotopic composition and elemental abundances exhibit high spatial heterogeneity and are dependent on the physical characteristics of different basins, not unlike the zones of similar influence model currently utilized to describe modern Florida Bay. Additionally, Florida Bay sediments preserve a record of major climate disturbance over the centurial time scale. Sediment geochemistry was found to record incidence of major storms of the last century, but again, the expression of the geochemical impacts varies with location and presumably hydrodynamic regime.

5.4 FUTURE STUDIES

The unifying feature of the isotopic data presented here is the high level of variability exhibited on all time scales, from isolated instances of process level variability in POM isotopic composition through seasonal and more widespread spatial variations in

POM to the geochemical imprint of anthropogenic and climatic events over the course of the last century. As such, this work presents a myriad of potential avenues for future geochemical study. From the process perspective, further work examining other indicators of N-fixation, such as nitrogenase enzymatic assays or mesocosm experimentation measuring uptake of isotopically labeled N_2 gas, is needed to elucidate the role fixed nitrogen plays in South Florida coastal environments. Additionally, given linkages evident in sedimentary records from several ocean basins, including the nearby Bahamas Banks setting (Ren et al. 2008), between N-fixation and denitrification in both modern and sedimentary records, it seems the poor understanding of denitrification in the various environments of the Everglades-mangrove ecotone-estuary-reef continuum of the South Florida coastal zone is a significant missing portion in understanding of the local nitrogen cycle. From the seasonal perspective, it is abundantly clear that the high level of spatial heterogeneity in POM from the coastal zone seen in this study of just ten locations in Florida Bay and the Florida Keys national Marine Sanctuary could be expanded to a more comprehensive list of locations, perhaps with greater coverage in hydrodynamic zones unassessed in the present study. Additionally, quarterly sampling resolution is insufficient to fully characterize seasonal variation, due to temporally isolated impacts of weather patterns and tidal influences. Higher sampling resolution might allow better correlation between water quality parameters and changes in POM geochemical character.

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APPENDICES

Appendix 1: Water Quality Data* for POM Time-series Sites

Station	Date	NO ₃ ⁻ (μM)	NH ₄ ⁺ (μM)	SRP (μM)	CHL-A (mg/L)	Salinity	Temp. (°C)
215	2002.65	0.028	0.128	0.022	0.044	36.48	30.49
	2003.09	0.155	0.209	0.015	0.126	35.52	18.84
	2003.33	0.388	0.536	0.021	0.082	35.42	26.01
	2003.60	0.054	0.190	0.029	0.033	36.20	31.13
	2003.80	0.307	0.144	0.025	0.106	34.92	27.73
	2004.11	0.104	0.267	0.010	0.158	36.33	22.26
	2004.43	0.043	0.164	0.031	0.082	36.83	30.54
	2004.63	0.062	0.116	0.018	0.000	36.63	31.05
	2004.80	0.000	0.119	0.049	0.043	36.209	26.721
	2005.09	0.000	0.864	0.039	0.157	36.738	20.645
225	2002.66	0.142	0.218	0.050	0.014	36.06	29.70
	2003.09	0.049	0.149	0.051	0.200	36.32	21.85
	2003.34	0.409	0.411	0.059	0.002	36.06	26.99
	2003.61	0.037	0.218	0.015	0.016	35.30	30.48
	2003.80	0.374	0.179	0.053	0.106	35.82	28.24
	2004.11	0.004	0.230	0.014	0.189	36.15	24.60
	2004.44	0.043	0.148	0.038	0.000	36.48	28.18
	2004.65	0.137	0.458	0.010	0.000	35.45	30.30
	2004.80	0.123	0.048	0.014	0.078	35.970	28.143
	2005.09	0.270	0.378	0.017	0.011	36.474	23.474
243	2002.68	0.002	0.195	0.035	0.120	36.63	30.45
	2003.11	0.704	1.485	0.084	0.335	35.53	23.09
	2003.38	0.093	0.182	0.094	0.269	36.47	28.31
	2003.69	0.037	0.015	0.040	0.266	35.44	29.82
	2003.82	0.071	0.239	0.134	0.179	35.96	27.85
	2004.13	0.155	1.567	0.035	0.408	35.90	23.04
	2004.42	0.025	0.218	0.039	0.043	36.39	28.52
	2004.65	0.043	1.192	0.021	0.000	35.50	30.61
	2004.84	0.187	0.263	0.038	0.000	36.251	27.971
	2005.13	1.165	1.759	0.033	0.000	36.472	23.009
248	2002.68	0.102	0.190	0.024	0.161	36.20	30.22
	2002.83	0.056	0.442	0.048			
	2003.11	0.546	1.003	0.108	0.323	35.00	22.54
	2003.39	0.116	0.341	0.038	0.113	36.58	28.83
	2003.63	0.104	0.111	0.025	0.030	35.28	30.29

Station	Date	NO ₃ ⁻ (μM)	NH ₄ ⁺ (μM)	SRP (μM)	CHL-A (mg/L)	Salinity	Temp. (°C)
248	2004.25	0.314	0.200	0.002	0.023	36.38	24.43
Cont.	2004.42	0.052	0.306	0.029	0.039	36.50	28.43
	2004.65	0.082	0.317	0.020	0.098	35.51	30.71
	2004.84	0.016	0.041	0.023	0.082	36.279	27.386
	2005.13	0.442	1.395	0.034	0.035	36.624	22.225
255	2002.69	0.191	0.666	0.039	0.370	36.35	29.62
	2003.17	0.311	0.400	0.059	0.238	35.43	26.79
	2003.42	0.262	0.295	0.074	0.186	36.47	30.02
	2003.75	0.089	0.295	0.017	0.134	35.76	29.71
	2003.86	0.682	0.141	0.014	0.321	34.85	26.28
	2004.25	0.090	0.611	0.018	0.110	36.45	24.20
	2004.40	0.000	0.165	0.015	0.000	36.77	27.64
	2004.82	0.047	0.067	0.043	0.094	36.103	27.463
	2005.07	0.000	0.740	0.075	0.000	36.462	22.756
284	2002.69	0.031	0.199	0.018	0.435	37.09	27.83
	2002.85	0.058	0.282	0.000	0.264	38.32	25.96
	2003.17	0.096	0.238	0.030	0.255	34.56	27.42
	2003.42	0.146	0.285	0.025	0.096	35.39	29.97
	2003.75	0.195	0.111	0.048	0.273	36.16	29.68
	2003.86	0.000	0.279	0.084	0.359	36.35	26.42
	2004.21	0.007	0.202	0.010	0.000	34.90	24.31
	2004.36	0.041	0.265	0.022	0.000	36.47	26.07
	2004.59	0.031	0.170	0.037	0.133	35.62	29.92
	2005.07	0.399	0.580	0.014	1.757	35.424	18.125
287	2002.69	0.035	0.320	0.011	0.620	36.45	27.90
	2002.85	0.061	0.298	0.002	0.220	38.36	26.30
	2003.17	0.093	0.324	0.073	0.191	34.70	27.55
	2003.42	0.260	0.377	0.064	0.137	35.59	29.97
	2003.75	0.081	0.070	0.040	0.505	36.80	29.65
	2003.86	0.019	0.135	0.037	0.151	36.94	26.24
	2004.21	0.018	0.136	0.002	0.134	34.93	24.11
	2004.36	0.030	0.500	0.023	0.000	36.26	25.75
	2004.59	0.142	0.147	0.025	0.453	36.45	30.04
	2005.07	0.010	0.250	0.022	0.979	35.160	17.835
BA	2002.79	0.165	2.520	0.019	0.491	33.61	29.99

Station	Date	NO ₃ ⁻ (μM)	NH ₄ ⁺ (μM)	SRP (μM)	CHL-A (mg/L)	Salinity	Temp. (°C)
BA Cont.	2003.07	0.129	1.337	0.049	0.435	34.62	15.11
	2003.19	0.087	2.773	0.072	0.705	35.74	28.18
	2003.44	1.780	2.002	0.088	1.438	34.64	29.85
	2003.69	0.134	2.963	0.013	1.233	35.71	31.81
	2004.05	0.194	2.208	0.008	0.285	28.46	20.32
	2004.22	0.164	0.700	0.029	0.914	33.42	23.16
	2004.49	0.596	0.809	0.041	0.937	43.95	31.80
	2004.74	0.077	2.771	0.008	0.459	38.39	30.08
	2004.82	0.298	4.216	0.025	0.700	41.71	26.12
	2005.06	0.178	1.404	0.054	0.459	41.68	16.93
DK	2002.71	0.888	1.266	0.133	0.408	24.36	30.07
	2003.07	3.043	5.430	0.039	0.156	28.07	14.57
	2003.19	5.200	7.587	0.063	0.306	29.99	28.05
	2003.44	1.108	4.145	0.038	0.337	31.11	29.35
	2003.68	1.612	4.261	0.281	0.521	16.76	29.85
	2004.06	1.243	4.435	0.012	0.149	25.71	19.17
	2004.24	0.900	1.768	0.016	0.170	30.24	23.66
	2004.49	0.589	0.955	0.045	0.218	38.57	30.11
	2004.74	1.687	16.967	0.028	0.502	38.60	29.16
	2005.07	2.508	8.415	0.030	0.328	38.33	15.76
SP	2002.71	0.064	0.234	0.043	1.081	30.13	3.38
	2003.07	0.294	0.220	0.030	1.299	14.31	9.37
	2003.19	0.222	0.318	0.096	0.476	27.91	1.39
	2003.44	0.416	0.468	0.061	0.413	30.13	1.41
	2003.69	0.063	0.218	0.031	0.708	30.25	2.80
	2004.05	0.098	0.388	0.017	0.410	19.65	1.87
	2004.22	0.398	0.177	0.021	0.486	23.37	3.39
	2004.49	0.680	0.204	0.040	0.463	31.01	1.96
	2004.74	0.059	0.127	0.014	0.740	28.56	2.07
	2005.06	0.054	1.128	0.072	1.515	16.79	9.675

* Data were provided by the SERC-FIU Water Quality Monitoring Network which is supported by SFWMD/SERC Cooperative Agreement #4600000352 as well as EPA Agreement #X7-96410603-3.

Appendix 2: Element and Stable Isotope Data from Three POM Size Fractions

Size Fraction		0.1-50μM					50-150μM					>150μM				
Site	Quarter	%N	%C	δ ¹⁵ N (‰ AIR)	δ ¹³ C (‰ PDB)	C:N	%N	%C	δ ¹⁵ N (‰ AIR)	δ ¹³ C (‰ PDB)	C:N	%N	%C	δ ¹⁵ N (‰ AIR)	δ ¹³ C (‰ PDB)	C:N
215	Sept. 2002	n.s						25.04		-24.70		2.520		6.45		
	Jan. 2003	0.017	0.110	7.68	-24.29	7.4	1.03	16.25	4.35	-23.60	18.4	4.255	31.234	4.70	-22.69	8.6
	Mar. 2003	0.012	0.070	3.56	-25.06	6.9	1.80	7.79	4.20	-21.29	5.1	7.587	33.460	5.85	-23.77	5.1
	Jun. 2003	0.010	0.250	2.48	-23.36	28.1	1.61	22.88	3.02	-21.39	16.6	1.417	24.031	3.86	-23.76	19.8
	Sept. 2003	0.014	0.450	2.99	-23.91	37.2	1.73	18.26	3.39	-18.91	12.3	3.598	3.280	3.89	-23.43	1.1
	Jan. 2004	0.013	0.100	5.71	-24.46	9.1	1.44	19.58	3.66	-17.93	15.8	6.483	8.370	4.56	-23.89	1.5
	Mar. 2004	0.008	0.050	4.25	-22.06	7.4	0.39	4.22	3.06	-16.37	12.6	3.942	31.790	3.69	-17.07	9.4
	Jun. 2004	0.011	0.050	3.06	-22.48	5.1	1.99	7.69	5.29	-20.07	4.5	4.523	26.875	4.09	-18.75	6.9
	Sept. 2004	0.011	0.050	3.14	-21.81	5.5	1.48		3.50			5.871	4.250	4.50	-22.10	0.8
	Jan. 2005	0.010	0.070	3.08	-23.39	8.2			3.24				15.490	2.70	-19.40	
225	Sept. 2002	n.s					1.57	41.34	4.07	-24.96	30.7	2.067	37.228	3.68	-18.82	21.0
	Jan. 2003	0.011	0.060	5.03	-24.99	6.6	1.51	16.87	4.01	-19.67	13.0	6.721	11.700	4.58	-23.67	2.0
	Mar. 2003	0.026	0.060	3.89	-22.39	2.7	2.96	17.42	4.07	-19.81	6.9	7.747	7.380	7.44	-19.45	1.1
	Jun. 2003	0.023	0.150	6.06	-23.92	7.8	2.73	18.49	3.61	-20.11	7.9	7.601	27.480	4.78	-20.63	4.2
	Sept. 2003	0.011	0.080	1.90	-25.70	8.4	0.86	16.53	2.27	-14.78	22.6	2.742	35.035	2.35	-13.16	14.9
	Jan. 2004	0.010	0.050	4.32	-23.39	5.6	0.95	9.86	3.37	-21.54	12.1	7.413	32.610	5.02	-23.60	5.1
	Mar. 2004	0.010	0.060	2.75	-22.04	7.3	0.70	16.09	2.75	-15.69	26.7	4.463	41.100	3.78	-16.85	10.7
	Jun. 2004	0.012	0.060	3.79	-21.58	5.6	1.12		1.89			2.766	42.760	2.23	-17.14	18.0
	Sept. 2004	0.012	0.080	3.13	-23.64	7.5	1.30	22.72	3.25	-18.57	20.4	4.240	25.530	4.36	-15.66	7.0
	Jan. 2005	0.010	0.070	3.30	-24.05	8.2			2.45				22.090	3.38	-13.12	
243	Sept. 2002	n.s					1.55	24.33	3.01	-19.13	18.3	5.713	43.706	3.89	-19.92	8.9
	Jan. 2003	0.006	0.110	6.41	-24.3	20.3	2.20		5.56			4.821	32.122	4.71	-21.01	7.8
	Mar. 2003	0.016	0.060	2.62	-23.8	4.5	2.07	2.80	4.45	-21.62	1.6	6.894	15.570	6.55	-24.06	2.6
	Jun. 2003	0.017	0.090	3.33	-22.5	6.1	3.48	5.40	3.92	-19.97	1.8	2.892	42.403	4.33	-22.52	17.1
	Sept. 2003	0.017	0.310	2.64	-23.6	20.7	2.28	10.51	3.71	-24.60	5.4	3.747	30.395	4.20	-21.73	9.5
	Jan. 2004	0.010	0.380	1.98	-25.5	45.8	0.40	9.89	2.91	-16.91	28.6	2.630	22.380	3.38	-16.74	9.9
	Mar. 2004	0.011	0.060	2.67	-23.2	6.4	1.75	11.68	3.44	-23.37	7.8	3.431	13.420	3.45	-22.73	4.6
	Jun. 2004	0.010	0.050	2.31	-22.5	5.9	1.48	7.41	2.75	-19.55	5.8	3.965	29.155	1.35	-19.84	8.6

Site	Quarter	%N	%C	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C:N	%N	%C	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C:N	%N	%C	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C:N
	Sept. 2004	0.018	0.080	3.41	-21.6	5.3	3.71	18.24	3.97	-18.89	5.7	6.165	39.260	5.05	-22.50	7.4
	Jan. 2005	0.010	0.080	3.11	-23.5	9.3			2.58				13.750	4.70	-17.98	
248	Sept. 2002	n.s					2.15	24.02	3.57	-18.40	13.0	1.574	23.237	4.78	-15.75	17.2
	Jan. 2003	0.011	0.080	2.01	-23.9	8.3	1.25	7.31	3.64	-19.71	6.8	6.512	31.557	4.34	-19.53	5.7
	Mar. 2003	0.017	0.100	2.68	-24.1	6.9	2.55	9.38	4.80	-24.34	4.3	4.830	25.220	4.81	-14.37	6.1
	Jun. 2003	0.011	0.090	1.54	-23.3	9.2	4.03	16.46	4.13	-20.28	4.8	1.858	23.660	3.60	-20.22	14.9
	Sept. 2003	0.011	0.170	1.55	-23.5	17.5	2.37	27.18	3.02	-18.62	13.4	2.973	26.724	4.11	-18.70	10.5
	Jan. 2004	0.024	0.060	2.26	-23	2.9	1.06	24.32	2.28	-13.10	26.8	3.737	38.500	4.10	-15.61	12.0
	Mar. 2004	0.016	0.070	2.89	-22	5.1	1.84	13.37	3.58	-16.94	8.5	3.370	22.540	3.86	-21.21	7.8
	Jun. 2004	0.015	0.080	1.46	-20.6	6.4	3.67	7.58	3.35	-18.36	2.4	4.142	28.510	5.07	-17.54	8.0
	Sept. 2004	0.015	0.090	2.74	-22.3	7.2	2.42	13.80	3.58	-15.27	6.6	4.296	39.260	4.52	-22.50	10.7
	Jan. 2005	0.020	0.120	3.77	-22.3	7.0			2.94				5.670	4.59	-23.70	
255	Sept. 2002	n.s														
	Jan. 2003	0.009	0.050	2.29	-23.9	6.2	2.26	10.85	3.98	-24.90	5.6	4.434	11.960	4.73	-23.87	3.1
	Mar. 2003	n.s					2.37	5.99	5.03	-19.96	2.9	2.221	28.035	3.28		14.7
	Jun. 2003	0.014	0.210	1.64	-23	17.3	4.01	20.57	4.02	-19.43	6.0	3.565	21.830	4.65	-21.70	7.1
	Sept. 2003	0.014	0.060	1.57	-22.3	5.0	2.31	10.95	3.46	-18.24	5.5	1.170	5.080	5.03	-19.91	5.1
	Jan. 2004	0.016	0.050	2.89	-24.6	3.6	2.72	11.31	3.23	-17.64	4.8	1.171	12.730	2.67	-13.04	12.7
	Mar. 2004	0.017	0.060	3.57	-21.7	4.2	0.65	15.43	3.18	-15.61	27.6	3.520	20.400	4.01	-14.29	6.8
	Jun. 2004	0.023	0.110	2.96	-20.3	5.5	2.56	16.07	3.81	-20.26	7.3	3.284	18.280	4.48	-19.74	6.5
	Sept. 2004	0.034	0.130	2.50	-19.3	4.5	4.00	16.63	3.97	-17.95	4.8	5.161	46.030	5.72	-26.80	10.4
	Jan. 2005	0.020	0.105	1.44	-21.39	6.1			3.74				9.550	5.47	-20.88	
284	Sept. 2002	n.s					2.46	8.56	4.28	-18.43	4.1	1.880	36.393	3.19	-18.97	22.6
	Jan. 2003	0.010	0.080	3.02	-23.2	9.4	1.46	14.18	3.40	-15.01	11.4	3.361	25.297	4.95	-20.06	8.8
	Mar. 2003	0.013	0.090	4.30	-21.5	8.1	1.47	16.79	3.83	-14.50	13.4	2.373	24.470	3.82	-11.97	12.0
	Jun. 2003	0.013	0.080	3.28	-20.7	7.4	2.01	9.61	3.86	-14.90	5.6	1.339	19.540	1.99	-12.25	17.0
	Sept. 2003	0.028	0.090	3.47	-19.77	3.7	2.78	18.61	3.48	-14.91	7.8	1.088	17.670	2.64	-10.62	18.9
	Jan. 2004	0.026	0.080	1.66	-23.9	3.6	1.52	7.92	4.42	-20.06	6.1	2.192	25.310	3.73	-15.91	13.5
	Mar. 2004	0.029	0.100	3.37	-19.7	4.0	2.51	21.99	3.63	-15.28	10.2	1.870	23.770	3.16	-12.64	14.8
	Jun. 2004	0.020	0.080	4.47	-20.5	4.7	3.75	16.33	4.75	-20.07	5.1	6.887	9.070	8.39	-19.36	1.5
	Sept. 2004	0.028	0.140	2.38	-18.4	5.7	2.28	9.15	3.96	-14.93	4.7	1.613	14.280	3.09	-11.72	10.3
	Jan. 2005	0.015	0.115	2.31	-22.56	8.9			3.92				27.690	4.07	-12.72	

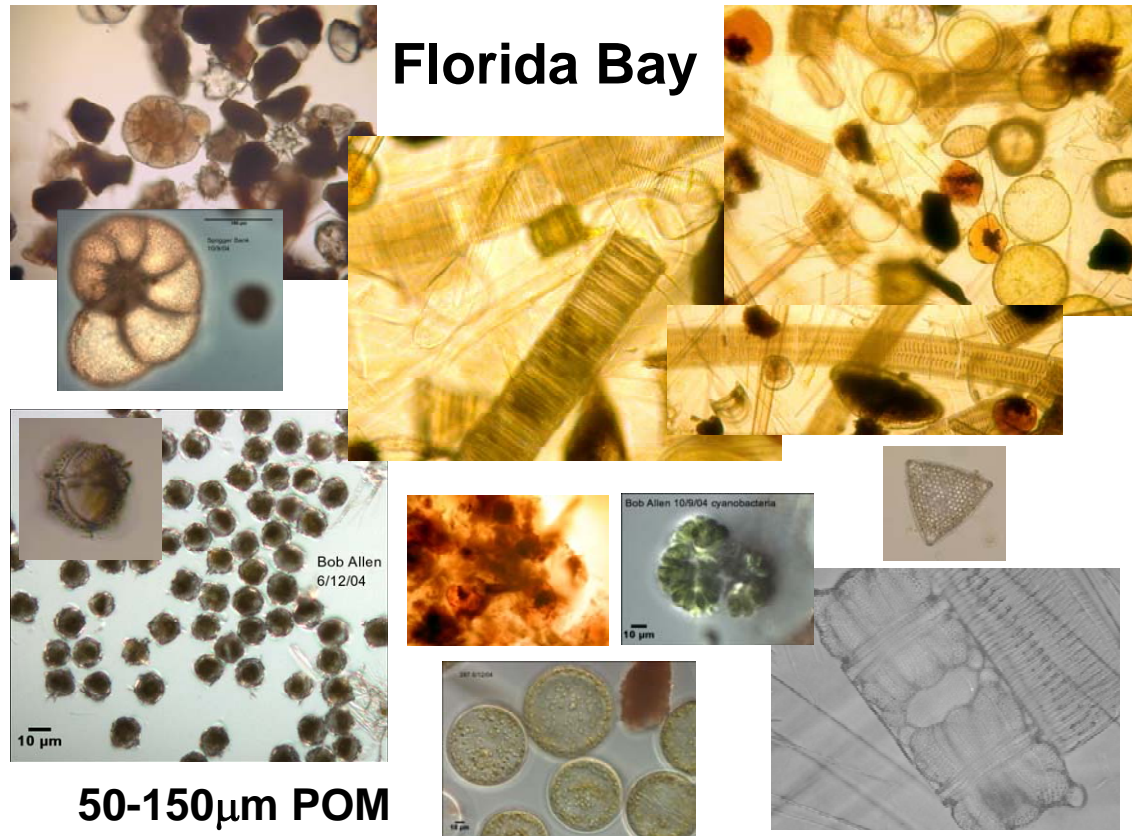
Site	Quarter	%N	%C	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C:N	%N	%C	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C:N	%N	%C	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C:N
287	Sept. 2002	n.s					1.51	9.18	4.01	-17.28	7.1					
	Jan. 2003	n.s					0.88	11.29	3.39	-14.90	15.0	2.415	24.310	4.19	-20.31	11.7
	Mar. 2003	0.012	0.120	1.09	-22.1	12.0	1.75	13.33	3.93	-16.05	8.9	3.711	7.170	4.97	-16.63	2.3
	Jun. 2003	0.017	0.100	2.10	-21.9	6.9	2.06	10.46	3.87	-15.43	5.9	1.240	5.490	2.49	-14.33	5.2
	Sept. 2003	0.02	0.15	2.3	-22.9	8.8	2.02	12.26	3.83	-13.76	7.1	1.464	21.360	2.26	-7.40	17.0
	Jan. 2004	0.037	0.260	2.52	-24.2	8.3	0.70	6.16	2.78	-15.40	10.2	8.156	33.026	4.54	-18.47	4.7
	Mar. 2004	0.025	0.070	2.05	-20.2	3.3	2.50	12.76	3.49	-15.82	6.0	1.446	20.250	2.22	-13.73	16.3
	Jun. 2004	0.034	0.170	2.94	-17.8	5.9	2.93	13.20	4.38	-19.96	5.3	1.695	16.380	3.81	-20.65	11.3
	Sept. 2004	0.017	0.090	2.27	-18.4	6.1	2.70	11.92	3.81	-16.06	5.2	2.873	9.250	3.66	-14.75	3.8
	Jan. 2005	0.020	0.115	1.94	-21.2	6.7			3.66			2.456	15.880	3.23	-14.48	7.5
SP	Sept. 2002	n.s					1.50	9.96	4.65	-18.27	7.7	0.856	39.620	3.58	-23.59	54.0
	Jan. 2003	0.025	0.060	4.60	-24.5	2.8	1.33	11.09	4.94	-17.11	9.7	3.945	26.850	4.65	-20.48	7.9
	Mar. 2003		0.130	4.05	-26		3.28	17.38	5.81	-18.88	6.2	1.757	26.400	4.48	-19.15	17.5
	Jun. 2003	0.017	1.070	3.51	-29.6	73.3	0.54	10.84	4.38	-15.76	23.5	1.033	19.590	2.80	-14.94	22.1
	Sept. 2003	0.026	0.480	2.44	-25.7	21.8	1.23	11.62	3.43	-14.29	11.0	2.119	27.860	1.97	-10.79	15.3
	Jan. 2004	0.038	0.210	3.21	-26.1	6.5	1.27	4.00	5.17	-25.58	3.7	0.892	4.310	4.19	-28.95	5.6
	Mar. 2004	0.060	0.280	1.57	-26.3	5.5	1.97	13.97	2.13	-12.91	8.3	2.681	30.910	3.54	-17.75	13.5
	Jun. 2004	0.030	0.150	3.06	-20.4	5.8	1.96	14.91	4.99	-19.99	8.9	4.302	10.730	5.09	-17.58	2.9
	Sept. 2004	0.028	0.090	2.78	-19.6	3.7	0.95	11.22	3.93	-15.65	13.8	3.363	22.000	3.57	-21.98	7.6
	Jan. 2005		0.410	4.60	-18.3				5.02							
BA	Sept. 2002	n.s					2.79		4.20			1.664	33.785	5.25	-25.41	23.7
	Jan. 2003	0.018	0.190	3.01	-22.1	12.3	1.53	25.26	5.07	-19.18	19.2	1.087	26.035	3.87	-25.02	27.9
	Mar. 2003	n.s					0.78	7.86	4.92	-15.51	11.7	0.860	15.166	4.12	-16.00	20.6
	Jun. 2003	0.033	0.130	2.71	-17.9	4.5	1.52	31.85	4.02	-14.84	24.5	4.223	7.245	5.58	-12.98	2.0
	Sept. 2003	0.091	0.250	2.99	-13.4	3.2	2.41	29.20	2.65	-16.92	14.1	0.705	11.430	3.80	-16.93	18.9
	Jan. 2004			2.70	-18		0.53	7.53	4.22	-13.87	16.7	0.911	10.654	4.10	-16.40	13.6
	Mar. 2004	0.080	0.200	2.42	-15	2.9	1.76	15.32	4.29	-14.31	10.1	1.354	29.970	4.05	-18.65	25.8
	Jun. 2004	0.118		2.23	-14		2.49	48.14	3.88	-13.80	22.6	1.766	7.340	3.76	-17.90	4.8
	Sept. 2004	0.086	0.460	3.28	-11.4	6.2	0.59	7.65	4.44	-13.46	15.1	2.104	31.349	4.83	-15.42	17.4
	Jan. 2005	0.160		3.26	-11.7				5.08							
DK	Sept. 2002	n.s					2.35	20.02	4.84	-18.92	9.9	0.253	28.237	8.51	-26.25	130.2
	Jan. 2003	0.015	0.160	4.09	-19.6	12.3	0.62	12.30	6.18	-19.80	23.2	2.264	21.488	6.33	-18.78	11.1

Site	Quarter	%N	%C	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C:N	%N	%C	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C:N	%N	%C	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C:N
	Mar. 2003	0.040		4.85	-25		0.29	8.51	6.08	-17.80	34.3	1.685	11.120	4.68	-20.85	7.7
	Jun. 2003	0.019	0.150	3.56	-18.8	9.4	1.19	30.59	4.68	-16.69	30.0	2.135	30.859	5.44	-20.47	16.9
	Sept. 2003	0.049	0.800	4.07	-24.8	19.2	2.03	32.10	2.31	-16.99	18.5					
	Jan. 2004	0.027	0.200	4.13	-19.4	8.8	0.88	10.57	6.00	-19.97	14.0	2.939	23.991	7.72	-16.76	9.5
	Mar. 2004	0.063	0.760	4.51	-26.7	14.1	1.76	18.60	6.34	-15.23	12.3	2.243	29.100	6.29	-16.17	15.1
	Jun. 2004	0.034	0.230	4.73	-18.3	7.8	1.35	17.76	6.75	-19.48	15.3	1.321	22.061	3.91	-23.35	19.5
	Sept. 2004	0.073	0.340	4.26	-15.0	5.4	0.51	6.93	5.70	-18.63	16.0	0.944	9.860	5.63	-21.98	12.2
	Jan. 2005		0.770	4.65	-13.0				5.97							

n.s – 0.1-50 μM size class was not sampled in Sept. 2002

* data gaps are due to insufficient sample for analysis

Appendix 3: Species assemblages in the 50-150 μ m size fraction of POM



Florida Bay assemblages were dominated by diverse group of diatom species, with lower abundances of benthic foraminifera, green microalgae, sediment particles, and organic detritus particles. Summer samplings showed a monospecific dinoflagellate bloom at interior/NE Florida Bay sites.



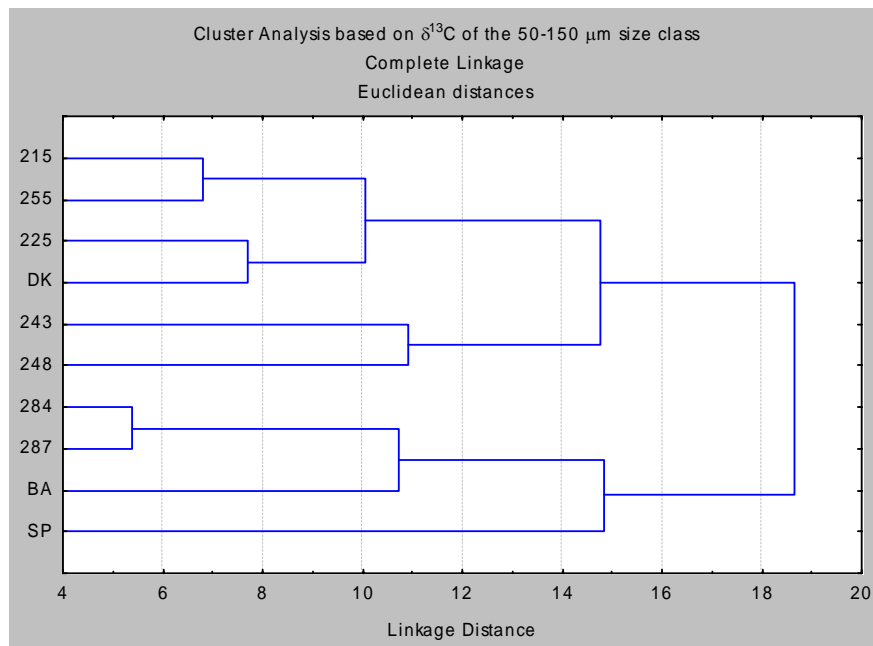
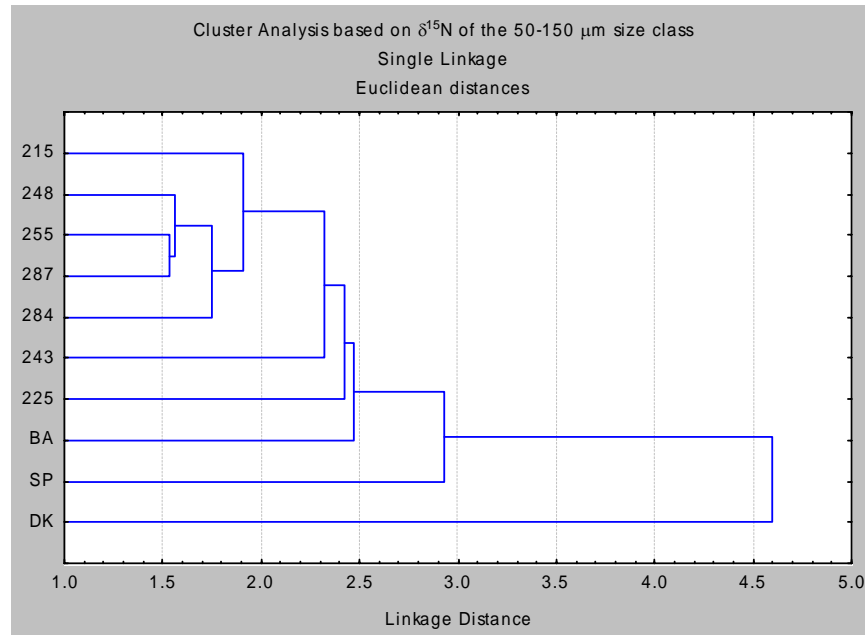
Atlantic Ocean site assemblages were composed of several species of the dinoflagellate genus, *Ceratium*, along with many species of both benthic and planktonic foraminifera. Amorphous organic gel and limited a limited diatom assemblage was also present. Additionally, the Atlantic sites had higher abundances of copepods and nauplii larvae.

Appendix 4: Particulate assemblages in the 50-150µm size fraction; bold shows dominant components

Site	Sampling Date							
	March 2003	June 2003	Sept. 2003	Jan. 2004	March 2005	June 2004	Sept. 2004	Jan. 2005
Carysfort reef	Dinoflag. <i>Ceratium</i> Few diatoms Amorphous-organics Forams	Green filaments Org. detritus Forams Few copepods Few diatoms Few dinoflag (<i>Ceratium</i>)	Org. Detritus <i>Ceratium</i> Few forams Green filaments	Sediment Org. detritus Few dinoflag. Few diatoms Few forams	Sediment copepods Few dinoflag. Few diatoms Few forams Green filaments	<i>Ceratium</i> <i>Protoperidinium</i> Filamentous org (little material)	Clear gel org. Forams Plant fragments No dinoflag No diatoms	Forams Detritus Copepods Sediments Organic fragments
Molasses Reef	Dinoflag. <i>Ceratium</i> <i>Peridinium</i> Few diatoms Green algae	Forams Dinoflag. <i>Ceratium</i> <i>Peridinium</i> Few diatoms Green algae	Org. Detritus <i>Ceratium</i> Few forams Green filaments	NS	Sediment Org detritus Org filaments Forams Copepods No dinoflag.	NS	Clear gel org. Few dinoflag. Few diatoms Few forams sediment	Org. detritus Few diatoms Few dinoflag Green algae
Tennessee Reef	Dinoflag. <i>Ceratium</i> <i>Peridinium</i> detritus	Dinoflag. <i>Ceratium</i> <i>Peridinium</i> Detritus copepods	Dinoflag. <i>Ceratium</i> <i>Peridinium</i> Detritus copepods	Sediment Benthic forams Coralling alg. Green algae	Benthic Forams Dinoflag. <i>Ceratium</i> detritus	Dinoflag. <i>Ceratium</i> detritus	Clear gel org. Few dinoflag. Few diatoms Few forams sediment	Forams Dinoflag. <i>Ceratium</i> <i>Peridinium</i> Plant fragments Few diatoms
Coffins Patch Channel	Dinoflag. <i>Ceratium</i> Copepods Few diatoms	Detritus Dinoflag. <i>Ceratium</i> Copepods	Forams Dinoflag. <i>Ceratium</i> <i>Peridinium</i> copepods Green algae	Sediment Org. detritus Forams Rare diatoms	Forams Dinoflag. <i>Ceratium</i> Detritus copepods Green algae	Forams Dinoflag. <i>Ceratium</i> copepods rare diatoms	Forams Dinoflag. <i>Ceratium</i> Detritus Clear gel org.	Forams Sediment Dinoflag. <i>Ceratium</i> Few diatoms.
Bahia Honda Channel	Diatoms Forams Dinoflag. Brown organics	Dinoflag “vase” Sediment Org. detritus Forams Few diatoms	Detritus Dinoflag. <i>Ceratium</i> <i>Peridinium</i> Forams Few diatoms	NS	Sediments Forams Rare <i>Ceratium</i> Rare diatoms	Forams Dinoflag. <i>Ceratium</i> copepods rare diatoms	Forams Dinoflag. <i>Ceratium</i> copepods diatoms detritus	Sediments Forams <i>Ceratium</i> diatoms

Tripod Bank	Diatoms forams	DIATOMS	DIATOMS Rhabdonema Forams	DIATOMS	DIATOMS	DIATOMS	DIATOMS	DIATOMS Org. detritus
Bamboo Bank	Diatoms forams	DIATOMS <i>Rhabdonema</i> <i>Rhizosolenia</i>	DIATOMS <i>Rhabdonema</i> forams	DIATOMS <i>Rhabdonema</i> <i>Rhizosolenia</i> <i>Campylodiscus</i> forams	DIATOMS <i>Rhabdonema</i> <i>Rhizosolenia</i> <i>Campylodiscus</i>	DIATOMS <i>Rhabdonema</i> <i>Rhizosolenia</i> <i>Campylodiscus</i> Green algae	DIATOMS <i>Rhabdonema</i> <i>Rhizosolenia</i> <i>Campylodiscu</i> <i>licomorphs</i>	DIATOMS Org. detritus
Sprigger Bank	NS	DIATOMS Detritus Sediment forams	DIATOMS Forams copepods	DIATOMS <i>Rhabdonema</i> <i>Rhizosolenia</i> <i>Coscinodiscus</i> Forams	DIATOMS Detritus Sediment forams	Fewer diatoms but still dominant Forams Clam larvae	DIATOMS Detritus Sediment forams	DIATOMS <i>Rhabdonema</i> <i>Rhizosolenia</i> <i>Coscinodiscus</i>
Bob Allen Bank	NS	Dinoflag BLOOM <i>Protoperidinium</i>	Dinoflag decaying <i>Protoperidinium</i>	DIATOMS Forams Some dinoflag.	Dinoflag <i>Protoperidinium</i> Detritus Sediments Diatoms Green algae	Dinoflag BLOOM <i>Protoperidinium</i>	Dinoflag decaying <i>Protoperidinium</i> Sediments Org. detritus Forams Green algae	Dinoflag decaying <i>Protoperidinium</i> Sediments Org. detritus Diatoms Forams Green algae
Duck Key	NS	Dinoflag BLOOM <i>Protoperidinium</i>	Dinoflag decaying <i>Protoperidinium</i> Forams	Dinoflag decaying <i>Protoperidinium</i> Forams	Diatoms Green algae Detritus dinoflag	Dinoflag BLOOM <i>Protoperidinium</i>	Dinoflag decaying <i>Protoperidinium</i> Sediments Green algae	Org. Detritus Forams Centric diatoms <i>Rhabdonema</i>

Appendix 5: Cluster analysis based on the isotopic values in the 50-150 μ m POM fraction.



Clustering based on $\delta^{13}\text{C}$ yielded 2 main groups, Florida Bay sites (SP, BA, 287, 284) and Atlantic Ocean sites (215, 225, 255, 243, 248); however Duck Key (DK) was

grouped with the Atlantic side. $D^{15}N$ values were able to separate the Florida Bay proper sites (Duck Key, Bob Allen Bank, and Sprigger Bank), however grouped the extreme western sites (284, 287) with the Atlantic Ocean sites.

Appendix 6: Trout Creek Core Geochemical Dataset

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
0-2	0.68	0.406	12.14	0.17	0.021	5.774	0.678	0.084	10.72	1.42	5.91	-19.64	9.9	177.2	17.8
2-4	0.73	0.440	12.08	0.15	0.013	5.621	0.671	0.059	10.81	1.28	6.47	-19.79	9.8	245.1	25.1
4-6	0.83	0.497	12.07	0.14	0.013	6.429	0.698	0.065	10.78	1.29	5.75	-19.79	10.7	256.8	23.9
6-8	0.73	0.439	12.16	0.13	0.011	6.749	0.590	0.049	10.63	1.54	6.17	-20.67	13.3	354.0	26.5
8-10	0.69	0.416	12.01	0.13	0.015	5.884	0.525	0.061	10.60	1.41	5.72	-19.73	13.1	248.4	19.0
10-12	0.85	0.513	11.91	0.12	0.012	6.523	0.590	0.064	10.63	1.27	6.44	-19.64	12.9	265.0	20.5
12-14	0.95	0.567	12.07	0.11	0.012	7.819	0.644	0.069	10.69	1.38	5.83	-20.20	14.2	292.9	20.7
14-16	0.74	0.443	12.10	0.12	0.012	6.370	0.536	0.055	10.67	1.44	6.62	-19.86	13.9	301.8	21.8
16-18	0.84	0.504	12.07	0.09	0.010	6.005	0.472	0.053	10.88	1.19	5.00	-20.32	14.9	294.1	19.8
18-20	0.46	0.278	12.05	0.10	0.042	3.366	0.277	0.116	10.84	1.21	7.58	-19.99	14.2	75.2	5.3
20-22	0.43	0.259	12.01	0.12	0.019	3.732	0.302	0.048	10.57	1.44	5.91	-19.50	14.4	199.9	13.9
22-24	0.98	0.590	12.24	0.13	0.010	11.245	0.766	0.060	10.34	1.91	5.33	-21.42	17.1	484.1	28.3
24-26	0.81	0.488	12.06	0.13	0.010	8.476	0.635	0.050	10.33	1.74	5.61	-19.26	15.6	438.3	28.1
26-28	0.85	0.508	12.04	0.13	0.010	9.868	0.671	0.049	10.10	1.94	5.98	-19.29	17.2	524.0	30.5
28-30	0.77	0.463	12.05	0.16	0.011	9.344	0.761	0.052	10.03	2.02	6.97	-19.21	14.3	459.9	32.1
30-32	0.63	0.380	11.97	0.13	0.007	7.198	0.495	0.027	10.08	1.89	5.85	-19.44	17.0	686.2	40.4
32-34	0.64	0.385	12.34	0.13	0.007	8.945	0.518	0.025	10.01	2.32	5.20	-20.10	20.1	919.4	45.6
34-36	0.67	0.405	12.32	0.13	0.006	9.225	0.528	0.026	10.04	2.28	5.88	-20.28	20.4	916.2	45.0
36-38	0.76	0.455	11.91	0.13	0.007	8.557	0.596	0.031	10.03	1.88	5.47	-19.88	16.8	713.5	42.6
38-40	0.65	0.389	11.99	0.14	0.006	7.612	0.531	0.022	10.03	1.96	5.85	-20.05	16.7	887.9	53.1
40-42	0.76	0.458	12.65	0.14	0.006	10.990	0.621	0.026	10.25	2.40	5.26	-21.26	20.7	1081.9	52.4
42-44	0.82	0.490	12.20	0.15	0.006	10.997	0.711	0.030	9.95	2.24	5.23	-20.51	18.0	938.1	52.0
44-46	0.84	0.506	12.04	0.14	0.006	10.436	0.693	0.030	9.98	2.06	5.54	-20.10	17.6	890.0	50.7
46-48	0.79	0.475	12.03	0.14	0.006	9.703	0.674	0.029	9.98	2.04	4.89	-19.67	16.8	867.5	51.6
48-50	0.97	0.583	12.13	0.14	0.004	11.810	0.804	0.026	10.10	2.03	4.91	-20.72	17.1	1188.9	69.4
50-52	0.86	0.516	11.95	0.13	0.004	9.493	0.647	0.022	10.11	1.84	4.74	-19.24	17.1	1138.1	66.5
52-54	0.72	0.435	11.96	0.12	0.004	7.910	0.537	0.018	10.14	1.82	5.14	-18.97	17.2	1110.3	64.6
54-56	0.78	0.468	11.95	0.12	0.004	8.623	0.574	0.020	10.10	1.84	4.85	-19.13	17.5	1124.3	64.1
56-58	0.66	0.396	11.66	0.11	0.004	5.609	0.453	0.017	10.24	1.42	5.34	-19.61	14.4	855.3	59.2

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
58-60	0.78	0.470	11.72	0.12	0.005	6.943	0.571	0.023	10.24	1.48	4.99	-19.52	14.2	790.9	55.7
60-62	0.92	0.552	11.67	0.11	0.004	8.465	0.632	0.024	10.14	1.53	5.47	-19.61	15.6	927.0	59.3
62-64	0.81	0.484	11.76	0.12	0.004	7.876	0.556	0.019	10.13	1.63	5.28	-19.38	16.5	1072.9	65.0
64-66	0.90	0.541	11.75	0.10	0.004	8.220	0.563	0.019	10.23	1.52	5.20	-19.39	17.0	1104.4	64.8
66-68	0.83	0.501	11.71	0.11	0.004	7.692	0.553	0.019	10.17	1.54	5.32	-18.68	16.2	1027.4	63.3
68-70	0.80	0.483	11.76	0.11	0.004	7.326	0.528	0.018	10.24	1.52	5.53	-19.42	16.2	1070.6	66.2
70-72	0.77	0.464	11.73	0.11	0.003	7.040	0.490	0.015	10.22	1.52	5.20	-19.48	16.8	1173.7	70.0
72-74	0.94	0.566	11.76	0.11	0.003	8.676	0.597	0.018	10.22	1.53	5.18	-19.62	17.0	1277.2	75.3
74-76	0.91	0.548	11.75	0.10	0.004	8.376	0.570	0.022	10.22	1.53	5.10	-19.32	17.1	978.4	57.1
76-78	0.98	0.591	11.66	0.09	0.004	7.848	0.550	0.026	10.33	1.33	5.07	-18.87	16.7	788.1	47.3
78-80	0.94	0.563	11.64	0.10	0.004	7.540	0.566	0.021	10.30	1.34	5.35	-19.78	15.5	932.2	60.0
80-82	0.92	0.551	11.64	0.10	0.003	7.351	0.523	0.017	10.31	1.33	5.77	-19.46	16.4	1094.7	66.8
82-84	0.90	0.540	11.57	0.08	0.004	6.280	0.448	0.022	10.40	1.16	5.88	-18.79	16.3	742.6	45.4
84-86	0.92	0.554	11.52	0.08	0.003	7.609	0.443	0.015	10.14	1.37	5.99	-18.43	20.0	1290.2	64.4
86-88	0.93	0.561	11.50	0.08	0.003	6.032	0.463	0.017	10.42	1.08	6.50	-18.79	15.2	908.4	59.7
88-90	0.86	0.516	11.51	0.08	0.004	4.967	0.410	0.019	10.55	0.96	6.27	-19.08	14.1	664.5	47.0
90-92	0.98	0.587	11.49	0.08	0.003	6.655	0.481	0.020	10.36	1.13	6.19	-18.94	16.1	868.9	53.9
92-96	1.28	0.766	11.34	0.09	0.004	9.424	0.663	0.028	10.11	1.23	5.84	-19.33	16.6	865.4	52.2

*MAR – Mass Accumulation Rate, expressed as $\text{g}/\text{cm}^2/\text{yr}$

**MAR expressed as $\text{mg}/\text{cm}^2/\text{yr}$

Appendix 7: Russell Bank Core Geochemical Dataset

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
0-2	0.77	0.852	11.98	0.25	0.009	20.269	2.159	0.079	9.59	2.38	4.77	-12.71	11.0	666.6	60.9
2-4	0.56	0.621	12.04	0.22	0.007	13.793	1.336	0.042	9.82	2.22	4.64	-12.63	12.0	858.4	71.3
4-6	0.50	0.548	12.27	0.23	0.008	12.502	1.286	0.043	9.99	2.28	4.44	-12.27	11.3	755.3	66.6
6-8	0.57	0.630	12.09	0.20	0.007	14.165	1.284	0.041	9.84	2.25	4.48	-12.23	12.9	892.1	69.3
8-10	0.61	0.669	12.15	0.21	0.007	15.596	1.399	0.045	9.82	2.33	4.55	-12.10	13.0	905.3	69.6
10-12	0.57	0.624	12.16	0.22	0.007	14.166	1.373	0.042	9.89	2.27	4.38	-12.24	12.0	865.2	71.9
12-14	0.68	0.751	12.07	0.19	0.006	14.500	1.424	0.047	10.14	1.93	4.86	-12.43	11.9	791.5	66.6
14-16	0.65	0.713	12.11	0.18	0.006	13.187	1.290	0.041	10.26	1.85	4.80	-12.24	11.9	834.9	70.0
16-18	0.62	0.680	12.08	0.19	0.005	13.260	1.278	0.035	10.14	1.95	4.77	-12.28	12.1	986.7	81.5
18-20	0.64	0.709	12.07	0.19	0.006	14.746	1.361	0.046	9.99	2.08	4.83	-12.11	12.6	835.8	66.1
20-22	0.64	0.701	12.06	0.20	0.006	14.937	1.395	0.044	9.92	2.13	5.01	-12.01	12.5	881.2	70.6
22-24	0.67	0.740	12.08	0.19	0.007	16.213	1.425	0.051	9.9	2.19	5.33	-12.01	13.3	817.2	61.6
24-26	0.65	0.713	12.10	0.19	0.006	13.682	1.382	0.043	10.18	1.92	5.21	-11.91	11.5	829.7	71.9
26-28	0.64	0.703	12.09	0.18	0.006	14.402	1.261	0.039	10.04	2.05	5.32	-11.97	13.3	952.1	71.5
28-30	0.57	0.631	12.22	0.21	0.006	14.257	1.350	0.039	9.97	2.26	4.93	-11.47	12.3	950.1	77.1
30-32	0.56	0.615	12.09	0.19	0.006	13.663	1.139	0.039	9.87	2.22	5.25	-11.76	14.0	900.3	64.3
32-34	0.53	0.579	12.12	0.20	0.007	13.672	1.185	0.039	9.76	2.36	5.68	-11.87	13.5	903.0	67.1
34-36	0.73	0.806	11.94	0.16	0.006	16.614	1.258	0.051	9.88	2.06	5.79	-12.11	15.4	845.0	54.8
36-38	0.74	0.811	12.00	0.16	0.006	15.248	1.294	0.047	10.12	1.88	5.70	-12.06	13.8	844.5	61.4
38-40	0.72	0.790	11.98	0.16	0.005	14.216	1.268	0.042	10.19	1.8	5.51	-11.94	13.1	875.0	66.9
40-42	0.77	0.845	12.05	0.16	0.005	15.541	1.351	0.044	10.21	1.84	5.46	-11.90	13.4	919.7	68.6
42-44	0.69	0.760	12.06	0.16	0.006	16.578	1.202	0.044	9.88	2.18	5.33	-11.87	16.1	978.9	60.8
44-46	0.79	0.869	12.10	0.15	0.006	18.940	1.342	0.049	9.91	2.18	5.37	-11.57	16.5	998.9	60.7
46-48	0.74	0.810	12.10	0.15	0.006	18.378	1.239	0.048	9.83	2.27	5.16	-11.50	17.3	999.5	57.7
48-50	0.81	0.890	12.13	0.16	0.006	20.124	1.411	0.052	9.87	2.26	4.92	-11.48	16.6	990.6	59.5
50-52	0.88	0.970	12.07	0.15	0.006	21.332	1.493	0.058	9.87	2.2	5.06	-11.50	16.7	945.8	56.7
52-54	0.84	0.926	12.08	0.16	0.006	20.566	1.478	0.059	9.87	2.22	5.21	-11.50	16.2	893.6	55.0
54-56	0.80	0.882	12.04	0.16	0.007	20.366	1.397	0.065	9.73	2.31	5.26	-11.65	17.0	808.8	47.6
56-58	0.79	0.870	12.02	0.16	0.006	25.222	1.352	0.055	9.12	2.9	5.05	-11.71	21.8	1191.2	54.7

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
58-60	0.76	0.834	11.97	0.15	0.007	16.683	1.239	0.055	9.97	2	5.78	-11.86	15.7	778.8	49.6
60-62	0.82	0.901	12.02	0.16	0.007	17.849	1.429	0.064	10.04	1.98	5.56	-11.64	14.6	718.9	49.3
62-64	0.78	0.854	12.05	0.16	0.006	19.381	1.328	0.051	9.78	2.27	5.70	-11.35	17.0	976.4	57.3
64-66	0.88	0.970	12.12	0.16	0.007	22.015	1.561	0.065	9.85	2.27	5.51	-11.67	16.4	871.9	53.0
66-68	0.85	0.940	12.16	0.17	0.007	22.187	1.603	0.067	9.81	2.36	5.37	-11.46	16.1	861.9	53.4
68-70	0.84	0.925	12.20	0.16	0.007	22.383	1.508	0.061	9.77	2.42	5.27	-11.45	17.3	943.9	54.5
70-72	0.94	1.034	12.13	0.16	0.008	23.567	1.664	0.079	9.85	2.28	5.34	-11.53	16.5	767.0	46.4
72-74	0.90	0.995	12.13	0.17	0.007	23.079	1.646	0.071	9.81	2.32	5.43	-11.35	16.4	842.5	51.5
74-76	0.89	0.979	12.13	0.16	0.007	22.125	1.571	0.067	9.87	2.26	5.21	-11.41	16.4	849.6	51.7
76-78	0.92	1.014	12.19	0.17	0.007	21.704	1.689	0.071	10.05	2.14	5.15	-11.24	15.0	785.5	52.4
78-80	0.94	1.029	12.21	0.17	0.007	23.038	1.774	0.070	9.98	2.24	5.04	-11.00	15.1	845.6	55.8
80-82	0.86	0.947	12.17	0.17	0.007	20.351	1.590	0.063	10.01	2.15	5.08	-11.01	14.9	840.2	56.3
82-84	0.90	0.995	12.16	0.17	0.007	18.801	1.686	0.070	10.26	1.89	5.14	-11.24	13.0	689.1	53.0
84-86	0.94	1.031	12.19	0.17	0.007	23.805	1.798	0.072	9.88	2.31	4.90	-11.20	15.4	849.5	55.0
86-88	0.91	0.996	12.22	0.18	0.007	22.619	1.799	0.071	9.95	2.27	5.03	-11.18	14.7	823.9	56.2
88-90	0.93	1.018	12.26	0.19	0.008	25.655	1.950	0.084	9.74	2.52	4.69	-10.95	15.4	787.4	51.3
90-92	0.82	0.901	12.23	0.18	0.008	20.721	1.631	0.070	9.94	2.3	4.88	-11.12	14.8	769.9	51.9
92-94	0.91	0.996	12.22	0.18	0.007	20.212	1.767	0.071	10.19	2.03	4.86	-11.00	13.3	735.5	55.1
94-96	0.91	1.004	12.23	0.17	0.007	22.689	1.752	0.072	9.97	2.26	5.20	-11.11	15.1	819.2	54.2
96-98	0.92	1.015	12.17	0.17	0.007	24.561	1.761	0.070	9.75	2.42	5.34	-10.84	16.3	905.6	55.7
98-100	0.84	0.921	12.16	0.17	0.007	18.694	1.570	0.065	10.13	2.03	5.59	-10.90	13.9	737.8	53.1
100-102	0.84	0.924	12.12	0.16	0.007	20.597	1.515	0.064	9.89	2.23	5.66	-10.98	15.9	828.3	52.2
102-104	0.94	1.035	12.16	0.15	0.006	21.427	1.542	0.066	10.09	2.07	5.69	-10.94	16.2	840.4	51.9
104-106	0.98	1.080	12.12	0.15	0.006	21.269	1.571	0.064	10.15	1.97	5.93	-10.66	15.8	863.1	54.6
106-108	0.96	1.052	12.14	0.15	0.005	19.570	1.541	0.057	10.29	1.86	5.86	-11.20	14.8	892.7	60.3
108-110	1.03	1.138	12.13	0.15	0.005	23.666	1.684	0.061	10.05	2.08	5.77	-10.78	16.4	996.9	60.8
110-112	0.98	1.083	12.15	0.15	0.006	22.637	1.630	0.064	10.06	2.09	5.48	-10.70	16.2	918.8	56.7
112-114	0.94	1.032	12.18	0.16	0.006	21.973	1.609	0.061	10.05	2.13	5.33	-10.96	15.9	924.5	58.0
114-116	0.90	0.988	12.18	0.16	0.006	21.348	1.542	0.058	10.01	2.16	5.28	-10.87	16.2	958.9	59.4
116-118	0.95	1.040	12.22	0.16	0.006	22.881	1.648	0.058	10.02	2.2	5.21	-10.71	16.2	1016.2	62.8
118-120	0.94	1.033	12.21	0.16	0.006	22.406	1.600	0.063	10.03	2.17	5.27	-10.71	16.3	923.3	56.5

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
120-122	0.88	0.973	12.19	0.16	0.007	19.856	1.543	0.065	10.15	2.04	5.23	-10.85	15.0	787.6	52.4
122-124	0.88	0.971	12.18	0.16	0.007	19.710	1.553	0.068	10.16	2.03	5.21	-10.87	14.8	746.5	50.4
124-126	1.01	1.110	12.19	0.16	0.006	23.982	1.788	0.070	10.03	2.16	5.23	-11.27	15.7	885.2	56.6
126-128	0.88	0.967	12.25	0.17	0.006	22.340	1.630	0.063	9.94	2.31	5.20	-10.82	16.0	922.2	57.7
128-130	0.94	1.029	12.23	0.17	0.006	22.421	1.702	0.064	10.05	2.18	5.19	-10.88	15.4	900.8	58.6
130-132	0.86	0.944	12.25	0.17	0.007	19.642	1.577	0.063	10.17	2.08	5.22	-10.68	14.5	802.7	55.2
132-134	1.02	1.127	12.17	0.16	0.007	22.764	1.764	0.074	10.15	2.02	5.24	-10.96	15.1	799.0	53.1
134-136	0.88	0.971	12.20	0.16	0.007	19.329	1.510	0.065	10.21	1.99	5.26	-11.03	14.9	772.4	51.7
136-138	0.91	1.004	12.17	0.16	0.007	20.291	1.617	0.065	10.15	2.02	5.36	-11.04	14.6	801.5	54.8
138-140	0.78	0.858	12.18	0.16	0.006	19.215	1.355	0.053	9.93	2.24	5.55	-10.64	16.5	944.7	57.1
140-142	0.83	0.912	12.20	0.17	0.006	21.612	1.523	0.058	9.83	2.37	5.28	-10.53	16.6	956.5	57.8
142-144	0.81	0.892	11.99	0.11	0.005	12.130	0.950	0.043	10.63	1.36	5.41	-10.67	14.9	723.1	48.5
144-146	0.78	0.863	11.66	0.09	0.004	7.936	0.738	0.035	10.74	0.92	5.32	-10.79	12.6	582.2	46.4
146-148	0.78	0.853	11.89	0.09	0.004	10.661	0.738	0.036	10.64	1.25	5.06	-10.62	16.9	773.7	45.9
148-150	0.88	0.970	12.03	0.13	0.004	15.620	1.300	0.042	10.43	1.61	5.02	-10.58	14.0	967.8	69.0
150-152	0.67	0.739	11.35	0.05	0.003	5.393	0.395	0.025	10.62	0.73	5.72	-11.14	15.9	552.6	34.7
152-154	0.81	0.895	12.03	0.13	0.006	13.870	1.123	0.050	10.48	1.55	5.35	-10.73	14.4	713.6	49.5
154-156	0.97	1.070	11.96	0.13	0.005	45.480	1.380	0.058	7.71	4.25	5.65	-10.50	38.4	2024.5	52.7
156-158	1.01	1.110	11.89	0.12	0.004	17.098	1.377	0.049	10.35	1.54	5.52	-10.82	14.5	894.1	61.7
158-160	0.88	0.963	12.05	0.12	0.004	13.777	1.132	0.038	10.62	1.43	5.44	-10.68	14.2	941.3	66.3
160-162	1.01	1.115	11.92	0.11	0.005	14.049	1.243	0.056	10.66	1.26	5.48	-10.83	13.2	650.1	49.3
162-164	1.20	1.324	11.85	0.09	0.004	14.829	1.205	0.050	10.73	1.12	5.36	-11.17	14.4	763.5	53.2
164-165	0.95	1.044	11.79	0.09	0.003	9.400	0.893	0.036	10.89	0.9	5.31	-11.32	12.3	672.5	54.8
core															
bottom	0.69	0.756	11.93	0.10	0.005	9.599	0.782	0.035	10.66	1.27	5.21	-11.30	14.3	712.4	49.8

*MAR – Mass Accumulation Rate, expressed as g/cm²/yr

**MAR expressed as mg/cm²/yr

Appendix 8: Bob Allen Bank Core Geochemical Dataset

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
0-2	0.56	0.224	12.19	0.22	0.007	5.620	0.493	0.016	9.68	2.51	3.89	-11.19	13.3	1015.5	76.3
2-4	0.53	0.212	12.13	0.22	0.007	5.281	0.466	0.015	9.64	2.49	3.75	-11.14	13.2	1008.2	76.3
4-6	0.7	0.28	12.29	0.22	0.007	6.823	0.616	0.020	9.85	2.44	4.21	-10.94	12.9	986.3	76.3
6-8	0.71	0.284	12.25	0.22	0.007	6.780	0.625	0.020	9.86	2.39	3.87	-10.72	12.7	966.3	76.3
8-10	0.64	0.256	12.26	0.21	0.006	6.063	0.538	0.015	9.90	2.37	4.35	-10.69	13.2	1118.3	85.0
10-12	0.68	0.272	12.20	0.2	0.007	6.440	0.544	0.019	9.83	2.37	4.89	-10.49	13.8	958.3	69.4
12-14	0.58	0.232	12.27	0.22	0.006	5.545	0.510	0.014	9.88	2.39	4.44	-10.41	12.7	1128.6	89.0
14-16	0.62	0.248	12.24	0.19	0.006	5.464	0.471	0.015	10.03	2.20	5.05	-10.60	13.5	1040.5	76.9
16-18	0.72	0.288	12.21	0.2	0.006	6.206	0.576	0.017	10.06	2.15	4.96	-10.53	12.6	1017.5	81.0
18-20	0.89	0.356	12.25	0.17	0.006	7.312	0.605	0.021	10.19	2.05	4.58	-10.56	14.1	970.0	68.8
20-22	0.73	0.292	12.39	0.2	0.005	6.751	0.584	0.015	10.07	2.31	4.91	-10.27	13.5	1310.1	97.1
22-24	0.7	0.28	12.24	0.18	0.005	3.568	0.504	0.014	10.97	1.27	4.62	-10.15	8.3	722.2	87.4
24-26	0.66	0.264	12.19	0.17	0.005	5.201	0.449	0.013	10.22	1.97	4.59	-10.08	13.5	1116.3	82.6
26-28	0.68	0.272	12.21	0.18	0.005	5.611	0.490	0.014	10.14	2.06	4.04	-9.73	13.4	1169.0	87.4
28-30	0.7	0.28	12.19	0.16	0.005	4.978	0.448	0.014	10.42	1.78	4.35	-9.41	13.0	1007.4	77.7
30-32	0.71	0.284	12.18	0.18	0.006	5.675	0.511	0.017	10.18	2.00	4.10	-9.69	13.0	943.6	72.9
32-34	0.81	0.324	12.26	0.19	0.006	6.890	0.616	0.019	10.14	2.13	4.34	-9.65	13.1	1004.1	76.9
34-36	0.71	0.284	12.25	0.19	0.006	6.116	0.540	0.017	10.10	2.15	3.87	-9.45	13.2	1017.0	76.9
36-38	0.71	0.284	12.19	0.19	0.006	5.914	0.540	0.017	10.10	2.08	4.03	-9.60	12.8	983.3	76.9
38-40	0.69	0.276	12.25	0.2	0.006	6.062	0.552	0.017	10.05	2.20	3.55	-9.51	12.8	1037.3	81.0
40-42	0.75	0.3	12.26	0.19	0.006	6.634	0.570	0.018	10.05	2.21	3.73	-9.44	13.6	1044.2	76.9
42-44	0.76	0.304	12.22	0.18	0.006	6.557	0.547	0.018	10.06	2.16	3.78	-9.39	14.0	1018.6	72.9
44-46	0.71	0.284	12.27	0.19	0.006	6.338	0.540	0.017	10.04	2.23	3.39	-9.31	13.7	1053.9	76.9
46-48	0.67	0.268	12.38	0.21	0.006	5.667	0.563	0.016	10.27	2.11	3.56	-9.27	11.7	998.5	85.0
48-50	0.64	0.256	12.22	0.17	0.006	6.036	0.435	0.015	9.86	2.36	3.86	-9.48	16.2	1113.4	68.8
50-52	0.79	0.316	12.20	0.18	0.006	5.314	0.569	0.019	10.52	1.68	3.80	-9.50	10.9	794.1	72.9
52-54	0.76	0.304	12.20	0.17	0.006	4.897	0.517	0.018	10.58	1.61	4.09	-9.57	11.1	760.6	68.8
54-56	0.77	0.308	12.23	0.18	0.007	4.601	0.554	0.022	10.73	1.49	4.29	-9.63	9.7	604.7	62.4
56-58	0.69	0.276	12.20	0.19	0.007	4.445	0.524	0.019	10.59	1.61	3.87	-9.56	9.9	651.9	65.9

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
58-60	0.68	0.272	12.33	0.21	0.007	6.534	0.571	0.019	9.93	2.40	4.26	-9.56	13.3	972.3	72.9
60-62	0.73	0.292	12.26	0.2	0.007	6.857	0.584	0.020	9.91	2.35	4.18	-9.61	13.7	950.6	69.4
62-64	0.91	0.364	12.13	0.17	0.007	7.253	0.619	0.025	10.14	1.99	4.12	-10.01	13.7	806.5	59.0
64-66	0.81	0.324	12.22	0.19	0.007	6.898	0.616	0.023	10.09	2.13	3.94	-9.83	13.1	861.7	65.9
66-68	0.78	0.312	12.17	0.18	0.007	6.370	0.562	0.022	10.13	2.04	4.14	-9.95	13.2	826.3	62.4
68-70	0.75	0.3	12.37	0.19	0.006	6.816	0.570	0.018	10.10	2.27	4.25	-9.42	14.0	1072.9	76.9
70-72	0.72	0.288	12.43	0.2	0.006	6.857	0.576	0.017	10.05	2.38	4.07	-9.20	13.9	1124.3	81.0
72-74	0.67	0.268	12.59	0.23	0.006	6.796	0.616	0.016	10.05	2.54	4.02	-8.88	12.9	1197.5	93.1
74-76	0.75	0.3	12.63	0.23	0.006	7.271	0.690	0.018	10.21	2.42	4.07	-8.59	12.3	1144.5	93.1
76-78	0.67	0.268	12.33	0.19	0.006	5.287	0.509	0.016	10.35	1.97	4.15	-8.94	12.1	931.6	76.9
78-80	0.77	0.308	12.36	0.19	0.006	6.609	0.585	0.018	10.21	2.15	3.74	-9.21	13.2	1013.2	76.9
80-82	0.65	0.26	12.36	0.18	0.006	5.459	0.468	0.016	10.26	2.10	3.73	-9.40	13.6	991.6	72.9
82-84	0.79	0.316	12.44	0.2	0.005	7.116	0.632	0.016	10.19	2.25	3.39	-9.25	13.1	1276.0	97.1
84-86	0.76	0.304	12.49	0.2	0.006	6.841	0.608	0.018	10.23	2.25	3.92	-9.15	13.1	1062.6	81.0
86-88	0.86	0.344	12.46	0.21	0.006	7.849	0.722	0.021	10.18	2.28	4.41	-9.15	12.7	1077.5	85.0
88-90	0.67	0.268	12.58	0.23	0.006	6.056	0.616	0.016	10.32	2.26	4.23	-9.38	11.5	1067.0	93.1
90-92	0.69	0.276	12.56	0.23	0.006	6.993	0.635	0.017	10.03	2.53	4.75	-9.16	12.9	1196.4	93.1
92-94	0.83	0.332	12.48	0.22	0.006	7.638	0.730	0.020	10.18	2.30	4.65	-9.01	12.2	1086.4	89.0
94-96	0.8	0.32	12.54	0.22	0.006	8.344	0.704	0.019	9.93	2.61	4.14	-9.04	13.8	1231.3	89.0
96-98	0.77	0.308	12.49	0.22	0.006	8.085	0.678	0.018	9.86	2.63	3.75	-9.20	13.9	1239.6	89.0
98-100	0.71	0.284	12.52	0.22	0.005	6.163	0.625	0.014	10.35	2.17	3.96	-9.11	11.5	1229.8	106.9
100-102	0.79	0.316	12.35	0.2	0.006	5.877	0.632	0.019	10.49	1.86	3.75	-9.21	10.8	878.3	81.0
102-104	0.78	0.312	12.43	0.21	0.005	6.172	0.655	0.016	10.46	1.98	3.87	-9.33	11.0	1120.9	102.0
104-106	0.83	0.332	12.52	0.22	0.005	6.887	0.730	0.017	10.44	2.07	3.79	-9.32	11.0	1175.5	106.9
106-108	0.75	0.3	12.42	0.22	0.006	6.326	0.660	0.018	10.31	2.11	3.93	-9.37	11.2	995.8	89.0
108-110	0.84	0.336	12.27	0.2	0.006	6.339	0.672	0.020	10.38	1.89	4.22	-9.60	11.0	890.9	81.0
110-112	0.98	0.392	12.23	0.19	0.007	7.414	0.745	0.027	10.33	1.89	4.12	-9.56	11.6	765.5	65.9
112-114	0.85	0.34	12.27	0.19	0.007	6.208	0.646	0.024	10.44	1.83	4.00	-9.42	11.2	739.1	65.9
114-116	0.93	0.372	12.29	0.17	0.006	6.350	0.632	0.022	10.58	1.71	3.69	-9.27	11.7	806.1	68.8
116-118	0.82	0.328	12.23	0.16	0.006	5.352	0.525	0.020	10.60	1.63	3.92	-9.41	11.9	770.5	64.8
118-120	0.87	0.348	12.17	0.16	0.006	6.905	0.557	0.021	10.19	1.98	3.98	-9.74	14.5	937.0	64.8

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
120-122	0.98	0.392	12.02	0.15	0.009	5.172	0.588	0.035	10.70	1.32	3.84	-10.89	10.3	415.4	40.5
122-124	0.98	0.392	11.99	0.13	0.008	4.216	0.510	0.031	10.92	1.08	3.95	-10.94	9.7	380.9	39.5
124-126	1	0.4	11.98	0.14	0.005	4.623	0.560	0.020	10.82	1.16	4.56	-10.23	9.6	654.9	68.0
126-128	1	0.4	11.91	0.12	0.004	3.175	0.480	0.016	11.11	0.79	4.62	-10.59	7.7	562.2	72.9
128-130	0.97	0.388	12.01	0.12	0.005	3.524	0.466	0.019	11.10	0.91	4.52	-10.50	8.8	514.7	58.3
130-132	0.85	0.34	12.05	0.14	0.006	4.099	0.476	0.020	10.85	1.21	4.54	-10.50	10.0	569.3	56.7
132-134	0.99	0.396	12.09	0.15	0.006	5.904	0.594	0.024	10.60	1.49	4.20	-10.66	11.6	704.0	60.7
134-136	1.04	0.416	12.13	0.15	0.006	6.551	0.624	0.025	10.55	1.57	4.33	-10.82	12.2	743.6	60.7
136-138	0.97	0.388	12.17	0.17	0.005	6.400	0.660	0.019	10.52	1.65	4.35	-10.65	11.3	934.7	82.6
138-140	1.06	0.424	12.08	0.16	0.005	6.613	0.678	0.021	10.52	1.56	4.36	-10.84	11.4	883.8	77.7
140-142	0.94	0.376	12.03	0.16	0.006	5.413	0.602	0.023	10.59	1.44	4.18	-10.92	10.5	679.8	64.8
142-144	0.99	0.396	12.08	0.15	0.005	5.265	0.594	0.020	10.75	1.33	4.72	-11.15	10.3	753.4	72.9
144-146	0.88	0.352	12.05	0.14	0.005	3.812	0.493	0.018	10.97	1.08	4.66	-10.79	9.0	613.6	68.0
146-148	1.16	0.464	12.06	0.13	0.005	5.792	0.603	0.023	10.81	1.25	4.62	-11.18	11.2	707.4	63.1
148-150	1.05	0.42	12.13	0.16	0.005	5.783	0.672	0.021	10.75	1.38	4.44	-10.85	10.0	780.3	77.7
150-152	0.92	0.368	12.11	0.14	0.005	4.855	0.515	0.018	10.79	1.32	4.77	-12.06	11.0	747.6	68.0
152-154	0.91	0.364	12.11	0.14	0.005	4.374	0.510	0.018	10.91	1.20	4.13	-11.40	10.0	680.9	68.0
154-156	0.97	0.388	12.20	0.15	0.004	5.812	0.582	0.016	10.71	1.50	4.23	-11.31	11.6	1061.0	91.1
156-158	0.91	0.364	12.17	0.15	0.005	5.245	0.546	0.018	10.72	1.44	4.04	-11.65	11.2	816.6	72.9
158-160	0.86	0.344	12.17	0.16	0.005	4.611	0.550	0.017	10.83	1.34	4.43	-12.55	9.8	759.5	77.7
160-162	0.95	0.38	12.13	0.16	0.005	5.271	0.608	0.019	10.74	1.39	3.95	-12.48	10.1	786.1	77.7
162-164	0.74	0.296	12.13	0.16	0.006	4.069	0.474	0.018	10.75	1.37	4.31	-12.93	10.0	649.2	64.8
164-166	0.76	0.304	12.15	0.17	0.005	5.165	0.517	0.015	10.45	1.70	4.01	-13.78	11.7	962.8	82.6
166-168	0.75	0.3	12.39	0.19	0.005	6.697	0.570	0.015	10.16	2.23	4.19	-15.15	13.7	1265.0	92.3
168-170	0.73	0.292	12.23	0.16	0.004	6.645	0.467	0.012	9.95	2.28	3.85	-15.47	16.6	1612.0	97.1
170-172	0.62	0.248	12.70	0.22	0.005	7.368	0.546	0.012	9.73	2.97	3.78	-17.51	15.8	1683.6	106.9
172-174	0.24	0.096	24.96	1.15	0.012	19.186	1.104	0.012	4.97	19.99	4.78	-23.69	20.3	4718.8	232.7
174-176	0.27	0.108	22.94	0.99	0.011	17.831	1.069	0.012	6.43	16.51		-24.01	19.5	4252.6	218.6
176-178	0.35	0.14	19.49	0.54	0.008	15.590	0.756	0.011	8.36	11.14	3.77	-24.03	24.1	3943.9	163.9
178-180	0.54	0.216	14.79	0.34	0.006	11.187	0.734	0.013	9.61	5.18	3.83	-23.06	17.8	2445.8	137.6
180-182	0.4	0.16	15.51	0.32	0.006	9.238	0.512	0.010	9.73	5.77	3.67	-24.02	21.0	2726.5	129.5

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
182-184	0.52	0.208	15.46	0.46	0.013	13.585	0.957	0.027	8.93	6.53	3.58	-23.10	16.6	1423.5	85.9
184-186	0.39	0.156	16.19	0.39	0.010	10.977	0.608	0.016	9.16	7.04	3.47	-23.23	21.0	1993.6	94.7
186-188	0.71	0.284	14.28	0.29	0.010	14.049	0.824	0.028	9.33	4.95	3.54	-21.43	19.9	1401.6	70.4
188-190	0.62	0.248	15.20	0.42	0.013	16.183	1.042	0.032	8.67	6.53	3.24	-22.90	18.1	1422.2	78.5
190-192	0.8	0.32	13.14	0.28	0.015	14.315	0.896	0.048	8.67	4.47	3.59	-20.04	18.6	845.0	45.3
192-193	1.12	0.448	13.26	0.41	0.033	32.378	1.837	0.148	6.03	7.23	4.17	-20.90	20.6	620.5	30.2
193- bottom	0.8	0.32	11.95	0.25	0.014	11.469	0.800	0.045	8.36	3.58	4.22	-17.14	16.7	725.4	43.4

*MAR – Mass Accumulation Rate, expressed as g/cm²/yr

**MAR expressed as mg/cm²/yr

Appendix 9: Ninemile Bank Core Geochemical Dataset

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
0-2	0.458	0.229	12.05	0.39	0.029	8.115	0.888	0.067	8.51	3.55	1.60	-13.50	10.7	312.9	29.3
2-4	0.576	0.288	12.02	0.35	0.032	8.799	1.005	0.092	8.97	3.05	1.60	-13.47	10.2	246.4	24.1
4-6	0.579	0.290	12.33	0.40	0.031	10.448	1.161	0.090	8.72	3.61	1.71	-13.70	10.5	298.8	28.4
6-8	0.722	0.361	12.63	0.42	0.027	14.380	1.515	0.099	8.65	3.99	1.49	-13.42	11.1	377.0	34.0
8-10	0.705	0.353	12.67	0.40	0.020	11.697	1.397	0.071	9.36	3.32	1.40	-11.74	9.8	423.0	43.3
10-12	0.539	0.270	12.49	0.39	0.020		1.052	0.054			1.48	-11.68			42.9
12-14	0.624	0.312	12.44	0.38	0.022	11.177	1.175	0.068	8.86	3.59	1.71	-11.60	11.1	421.8	38.0
14-16	0.466	0.233	12.24	0.37	0.019	8.416	0.852	0.045	8.63	3.61	1.71	-11.66	11.5	482.0	41.8
16-18	0.538	0.269	12.17	0.36	0.021	9.186	0.976	0.057	8.76	3.41	1.97	-11.98	11.0	416.0	37.9
18-20	0.750	0.375	12.18	0.30	0.017	10.872	1.126	0.063	9.29	2.90	1.90	-11.91	11.3	448.9	39.9
20-22	0.534	0.267	12.05	0.33	0.018	8.696	0.888	0.048	8.79	3.26	2.06	-11.87	11.4	470.4	41.2
22-24	0.533	0.266	12.22	0.33	0.018	8.473	0.890	0.048	9.04	3.18	1.93	-11.68	11.1	452.3	40.7
24-26	0.507	0.253	12.34	0.35	0.018	9.453	0.895	0.044	8.61	3.73	1.82	-11.34	12.3	549.8	44.6
26-28	0.552	0.276	12.27	0.34	0.017	9.512	0.943	0.046	8.82	3.45	1.94	-11.41	11.8	533.8	45.4
28-30	0.658	0.329	12.16	0.30	0.016	9.414	0.982	0.052	9.30	2.86	1.90	-11.48	11.2	467.6	41.8
30-32	0.706	0.353	12.11	0.27	0.013	9.711	0.951	0.045	9.36	2.75	1.88	-11.62	11.9	552.0	46.3
32-34	0.466	0.233	12.39	0.37	0.018	8.827	0.864	0.043	8.60	3.79	1.90	-10.84	11.9	533.3	44.8
34-36	0.504	0.252	12.39	0.37	0.018	9.249	0.921	0.046	8.72	3.67	2.00	-11.01	11.7	519.4	44.3
36-38	0.689	0.344	12.21	0.31	0.017	11.477	1.066	0.058	8.88	3.33	2.03	-11.39	12.6	508.7	40.5
38-40	0.580	0.290	12.27	0.33	0.024	10.414	0.966	0.068	8.68	3.59	1.99	-11.09	12.6	394.2	31.3
40-42	0.588	0.294	12.24	0.32	0.022	10.219	0.936	0.065	8.76	3.48	2.15	-11.23	12.7	408.2	32.1
42-44	0.648	0.324	12.23	0.32	0.019	10.443	1.051	0.062	9.01	3.22	2.07	-11.09	11.6	435.6	37.6
44-46	0.647	0.323	12.01	0.29	0.017	9.961	0.946	0.055	8.93	3.08	2.13	-10.75	12.3	467.5	38.1
46-48	0.745	0.373	12.09	0.29	0.017	10.897	1.081	0.062	9.16	2.92	1.99	-10.58	11.8	456.1	38.8
48-50	0.699	0.350	11.93	0.26	0.016	9.037	0.897	0.057	9.34	2.59	2.24	-10.82	11.7	412.5	35.1
50-52	0.694	0.347	11.95	0.28	0.020	10.394	0.962	0.069	8.95	3.00	2.24	-10.81	12.6	390.2	31.0
52-54	0.795	0.397	11.69	0.22	0.017	8.809	0.869	0.069	9.47	2.22	2.88	-11.84	11.8	331.2	28.0
54-56	1.104	0.552	11.50	0.16	0.017	10.623	0.901	0.093	9.57	1.92	3.10	-12.51	13.8	295.6	21.5
56-58	0.809	0.404	11.64	0.19	0.020	8.241	0.755	0.080	9.60	2.04	2.97	-12.11	12.7	265.5	20.8
58-60	0.807	0.404	11.70	0.20	0.020	9.500	0.816	0.081	9.35	2.35	2.76	-11.72	13.6	303.8	22.4
60-62	0.777	0.389	11.70	0.20	0.019	9.003	0.790	0.073	9.39	2.32	2.69	-11.88	13.3	319.2	24.0
62-64	0.683	0.341	11.85	0.24	0.017	8.524	0.820	0.058	9.35	2.50	2.48	-11.12	12.1	381.6	31.5

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
64-66	0.776	0.388	11.92	0.24	0.014	10.050	0.915	0.054	9.33	2.59	2.14	-10.76	12.8	483.2	37.7
66-68	0.763	0.382	11.89	0.25	0.016	10.751	0.951	0.059	9.07	2.82	2.23	-11.16	13.2	467.5	35.4
68-70	0.721	0.360	11.99	0.27	0.019	11.307	0.985	0.067	8.86	3.14	2.19	-10.89	13.4	437.0	32.6
70-72	0.645	0.323	11.99	0.28	0.019	9.293	0.909	0.063	9.11	2.88	2.15	-10.94	11.9	382.8	32.1
72-74	0.817	0.409	11.71	0.22	0.014	9.335	0.881	0.056	9.43	2.29	2.40	-11.48	12.4	427.5	34.6
74-76	0.696	0.348	11.88	0.23	0.018	9.367	0.795	0.064	9.19	2.69	2.27	-11.19	13.8	379.3	27.6
76-78	0.646	0.323	11.79	0.22	0.017	7.970	0.697	0.056	9.33	2.47	2.19	-11.05	13.3	370.8	27.8
78-80	0.794	0.397	11.84	0.19	0.015	8.556	0.747	0.058	9.68	2.16	2.57	-11.60	13.4	378.6	28.3
80-82	0.791	0.396	11.74	0.22	0.019	9.535	0.865	0.075	9.33	2.41	2.54	-11.73	12.9	329.3	25.6
82-84	0.570	0.285	11.82	0.20	0.015	6.198	0.568	0.041	9.64	2.17	2.52	-11.41	12.7	385.9	30.3
84-86	0.818	0.409	11.64	0.19	0.014	9.197	0.791	0.057	9.39	2.25	2.72	-12.04	13.6	413.8	30.5
86-88	0.813	0.406	11.72	0.20	0.015	8.330	0.801	0.061	9.67	2.05	2.75	-12.36	12.1	351.1	28.9
88-90	0.989	0.495	11.78	0.20	0.016	11.082	0.996	0.080	9.54	2.24	2.64	-11.83	13.0	356.3	27.4
90-92	0.837	0.418	11.73	0.17	0.013	8.271	0.723	0.056	9.75	1.98	2.88	-11.67	13.3	380.0	28.5
92-94	1.184	0.592	11.78	0.16	0.011	10.916	0.962	0.068	9.94	1.84	2.87	-11.71	13.2	414.3	31.3
94-96	1.048	0.524	11.82	0.16		9.808	0.831	0.000	9.95	1.87	2.64	-11.28	13.8		
96-98	0.740	0.370	11.84	0.20	0.012	8.419	0.736	0.046	9.56	2.28	2.68	-11.67	13.3	474.0	35.5
98-100	1.015	0.507	12.10	0.26	0.019	14.482	1.307	0.095	9.25	2.85	2.69	-11.02	12.9	392.3	30.3
100-102	0.950	0.475	11.81	0.22	0.021	12.004	1.036	0.100	9.29	2.53	3.01	-11.84	13.5	311.5	23.0
102-104	1.270	0.635	11.70	0.13	0.011	0.000	0.853	0.069			3.12	-12.51	0.0	0.0	27.4
104-106	1.540	0.770	11.65	0.11	0.012	8.312	0.882	0.092	10.57	1.08	3.31	-12.84	11.0	232.5	21.2
106-108	1.555	0.777	11.69	0.13	0.011	9.695	0.986	0.083	10.44	1.25	3.26	-13.25	11.5	300.0	26.1
108-110	1.448	0.724	11.74	0.11	0.011	7.304	0.766	0.081	10.73	1.01	3.03	-12.74	11.1	231.6	20.8
110-112	1.633	0.817	11.69	0.10		6.553	0.804	0.000	10.88	0.80	3.39	-12.43	9.5		
112-114	1.550	0.775	11.70	0.12	0.008	6.570	0.934	0.060	10.85	0.85	3.13	-12.35	8.2	280.9	34.2
114-116	1.124	0.562	11.76	0.15	0.016	8.324	0.826	0.091	10.28	1.48	2.66	-12.49	11.8	236.7	20.1
116-118	1.535	0.768	11.47	0.10	0.009	4.882	0.737	0.072	10.84	0.64	3.82	-12.79	7.7	176.0	22.8
118-120	1.411	0.705	11.68	0.08	0.008	5.133	0.579	0.057	10.96	0.73	3.78	-12.64	10.3	233.1	22.5
120-122	1.284	0.642	11.64	0.10	0.007	5.652	0.649	0.048	10.76	0.88	3.86	-12.26	10.2	304.0	29.9
122-124	1.415	0.707	11.68	0.08	0.006	6.417	0.590	0.046	10.78	0.91	4.00	-12.08	12.7	361.3	28.5
124-126	1.140	0.570	11.59	0.12	0.009	5.197	0.685	0.053	10.68	0.91	3.66	-12.58	8.9	254.9	28.8
126-128	1.224	0.612	11.67	0.10	0.008	6.564	0.602	0.048	10.60	1.07	3.93	-12.49	12.7	356.4	28.0
128-130	1.325	0.662	11.69	0.08	0.009	5.606	0.533	0.061	10.84	0.85	4.02	-13.50	12.3	236.7	19.3
130-132	0.941	0.471	11.61	0.10	0.009	5.077	0.459	0.043	10.53	1.08	3.77	-12.99	12.9	304.0	23.5

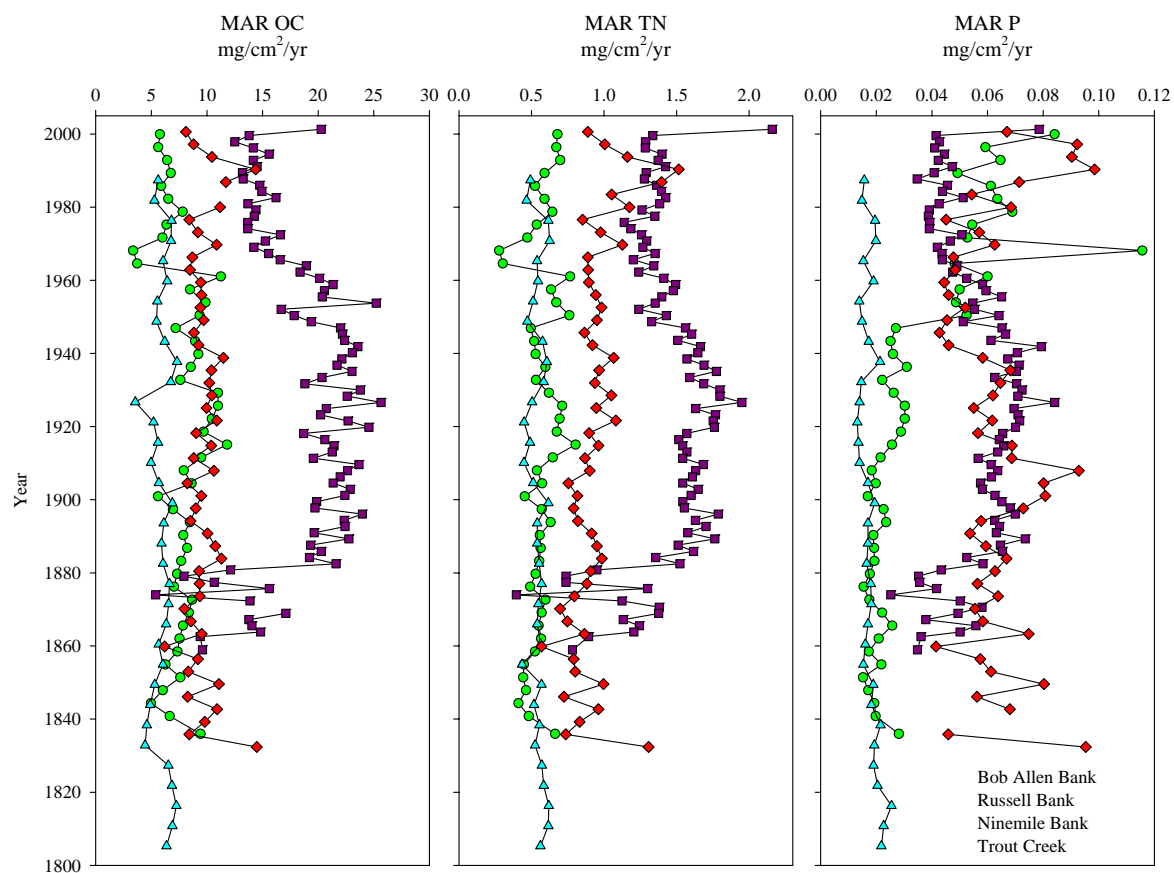
Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
132-134	1.065	0.532	11.63	0.10	0.009	6.331	0.523	0.045	10.44	1.19	3.80	-12.75	14.1	360.9	25.6
134-136	1.004	0.502	11.61	0.11	0.010	7.374	0.551	0.048	10.14	1.47	3.88	-12.34	15.6	394.3	25.2
136-138	1.299	0.650	11.68	0.10	0.009	7.878	0.661	0.060	10.47	1.21	4.12	-12.14	13.9	341.6	24.6
138-140	1.161	0.580	11.58	0.09	0.008	4.762	0.549	0.044	10.76	0.82	3.89	-13.02	10.1	280.9	27.8
140-142	1.020	0.510	11.64	0.09	0.007	5.153	0.484	0.036	10.63	1.01	3.85	-12.57	12.4	374.8	30.1
142-144	0.929	0.465	11.73	0.10	0.009	6.075	0.477	0.040	10.42	1.31	3.89	-12.27	14.9	389.0	26.2
144-146	1.152	0.576	11.65	0.10	0.008	7.015	0.568	0.049	10.43	1.22	3.84	-12.60	14.4	370.8	25.7
146-148	1.210	0.605	11.63	0.10	0.008	7.758	0.590	0.046	10.35	1.28	4.01	-11.98	15.4	434.7	28.3
148-150	1.373	0.687	11.57	0.11	0.010	0.000	0.738	0.070			3.94	-12.36			23.5
150-152	1.244	0.622	11.59	0.10	0.009	5.771	0.611	0.056	10.66	0.93	4.07	-12.56	11.0	267.7	24.3
152-154	0.736	0.368	11.77	0.09	0.005	4.002	0.346	0.019	10.68	1.09	3.80	-11.31	13.5	534.3	39.6
154-156	1.117	0.559	11.81	0.11	0.007	8.460	0.615	0.037	10.30	1.51	3.70	-11.30	16.0	583.7	36.4
156-158	0.992	0.496	11.72	0.11	0.007	7.823	0.569	0.033	10.15	1.58	3.73	-12.15	16.0	608.8	38.0
158-160	1.028	0.514	11.71	0.11	0.007	7.914	0.581	0.035	10.17	1.54	3.72	-11.99	15.9	587.1	36.9
160-162	0.980	0.490	11.70	0.11	0.007	6.883	0.541	0.035	10.30	1.40	3.81	-11.65	14.9	507.0	34.1
162-164	0.930	0.465	11.60	0.10	0.005	5.386	0.452	0.024	10.44	1.16	3.84	-11.93	13.9	574.1	41.3
164-166	1.223	0.611	11.57	0.08	0.006	6.873	0.500	0.036	10.45	1.12	4.07	-12.14	16.0	496.0	30.9
166-168	1.115	0.557	11.64	0.09	0.005	6.724	0.500	0.027	10.44	1.21	3.90	-12.15	15.7	654.4	41.7
168-170	1.108	0.554	11.61	0.09	0.007	7.165	0.508	0.037	10.32	1.29	3.88	-12.43	16.5	499.7	30.4
170-172	0.963	0.482	11.54	0.11	0.006	7.943	0.532	0.028	9.89	1.65	4.02	-12.47	17.4	736.7	42.3
172-174	0.956	0.478	11.42	0.10	0.005	6.499	0.464	0.022	10.06	1.36	4.19	-12.09	16.4	768.4	47.0
174-176	1.092	0.546	11.47	0.10	0.006	7.323	0.527	0.032	10.13	1.34	4.06	-12.60	16.2	584.6	36.1
176-178	0.830	0.415	11.49	0.09	0.004	5.744	0.381	0.018	10.10	1.38	3.93	-12.11	17.6	809.8	46.0
178-180	0.817	0.409	11.60	0.11	0.004	6.973	0.434	0.016	9.90	1.71	3.66	-11.84	18.7	1104.3	59.0
180-182	1.058	0.529	11.39	0.10	0.006	8.138	0.538	0.030	9.85	1.54	4.18	-12.19	17.7	704.2	39.9
182-184	0.930	0.465	11.41	0.10	0.006	6.047	0.474	0.028	10.11	1.30	4.04	-12.39	14.9	556.7	37.4
184-186	1.039	0.520	11.32	0.11	0.006	7.395	0.567	0.033	9.90	1.42	3.97	-12.27	15.2	574.2	37.7
186-188	1.002	0.501	11.49	0.12	0.006	10.226	0.584	0.030	9.45	2.04	3.69	-12.08	20.4	885.4	43.3
188-190	0.917	0.458	11.40	0.12	0.005	6.085	0.539	0.024	10.08	1.33	3.74	-12.38	13.2	663.5	50.3
190-192	0.921	0.461	11.42	0.11	0.006	9.732	0.521	0.027	9.31	2.11	3.95	-12.38	21.8	925.3	42.5
192-194	1.068	0.534	11.44	0.10	0.006	9.785	0.559	0.033	9.60	1.83	3.98	-11.97	20.4	774.2	37.9
194-196	0.974	0.487	11.45	0.11	0.005	10.387	0.547	0.027	9.32	2.13	4.04	-11.78	22.2	1007.3	45.4
196-198	1.075	0.538	11.53	0.12	0.006	10.846	0.638	0.031	9.51	2.02	3.76		19.8	901.9	45.5
198-200	0.956	0.478	11.54	0.12	0.005	9.265	0.584	0.025	9.61	1.94	3.36		18.5	957.7	51.8

Depth	Bulk Density (dry)	MAR*	%C	%N	%P	MAR- OC**	MAR- N**	MAR- P**	Total IC (%)	Total OC (%)	$\delta^{15}\text{N}$ (‰ AIR)	$\delta^{13}\text{C}$ (‰ PDB)	C/N	C/P	N/P
200-202	0.892	0.446	11.80	0.12	0.004	10.349	0.545	0.019	9.48	2.32	3.26	-11.48	22.1	1391.9	62.9
202-204	0.849	0.424	11.82	0.12	0.005	10.437	0.525	0.022	9.36	2.46	3.50	-11.68	23.2	1251.4	54.0
204-206	0.952	0.476	11.72	0.11	0.005	10.331	0.530	0.023	9.56	2.17	3.71	-12.06	22.7	1152.3	50.7
206-208	1.052	0.526	11.57	0.10	0.005	11.048	0.521	0.026	9.47	2.10	4.13	-12.19	24.7	1111.8	45.0
208-210	1.185	0.592	11.33	0.08	0.005	10.601	0.461	0.032	9.54	1.79	4.24	-13.15	26.8	858.5	32.0
210-212	1.298	0.649	11.30	0.08	0.006	10.775	0.498	0.037	9.64	1.66	4.84	-13.48	25.3	746.2	29.5
212-214	1.239	0.619	11.28	0.07	0.004	10.218	0.454	0.025	9.63	1.65	4.50	-13.47	26.2	1053.5	40.2
214-216	1.202	0.601	11.36	0.07	0.004	8.412	0.427	0.024	9.96	1.40	4.58	-13.63	23.0	918.6	40.0
216-218	1.302	0.651	11.40	0.07	0.003	9.049	0.427	0.021	10.01	1.39	4.38	-13.12	24.7	1127.3	45.6
218-220	1.013	0.506	11.48	0.08	0.007	8.049	0.398	0.034	9.89	1.59	4.58	-13.12	23.6	615.7	26.1
220-222	1.128	0.564	11.64	0.08	0.006	8.627	0.445	0.032	10.12	1.53	4.13	-13.02	22.6	700.7	31.0

*MAR – Mass Accumulation Rate, expressed as g/cm²/yr

**MAR expressed as mg/cm²/yr

Appendix 10: Florida Bay core elemental composition based on mass accumulation rate calculations. Organic carbon, total nitrogen and total inorganic phosphorus are shown.



VITA

SAMANTHA L. EVANS

- 1993-1998 Bachelor of Science (Geology), First Class Honours, St. Francis Xavier University, Antigonish, Nova Scotia, Canada; Honours Philip W. Oland Scholarship, St. Francis Xavier University, \$20K. St. Francis Xavier University Alumni Recognition Award for academic excellence and contribution to the St. Francis Xavier University community. Atlantic Universities Geology Conference; APICS Prize for best scientific paper. St. Francis Xavier University, Antigonish, Nova Scotia, Canada; Silver Medal: Highest academic average in the final three years of a degree program St. Francis Xavier University. Professor Donald J. MacNeil Memorial Award for outstanding graduating geology student.
- 1998-2000 Master of Science (Biology), Florida Atlantic University, Boca Raton, Florida, U.S.A.; Florida Atlantic University, Boca Raton, FL; Elsa Alvear Award for Excellence in Teaching.
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