Anthropogenic Changes Over The Last 100 Years In Dove Sound, Upper Florida Keys, USA

by

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Dedication:

This Graduate Thesis is dedicated to my family and to the varied members of my extended family who have encouraged, supported and endured my efforts along the way to completing this life goal, Thank you All!

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Abstract:

Dove Sound located near Key Largo, Florida (USA) was investigated to determine potential anthropogenic influences from landuse alteration such as highway and residential developments. The sediment load and nutrient flux was investigated using ^{210}*Pb dating of a sediment core, combined with stable isotope values* $\delta^{15}N$, $\delta^{13}C$ *and pigment analysis. A* ^{210}*Pb CRS model 130 year horizon was determined for the upper 12cm of the core. Mass sedimentation rates over this time period increased approximately 10 fold from 5.0 ±0.97 mg* $cm^{-2}\ yr^{-1}$ *(10-12cm depth interval) to 48.58±3.61 mg* $cm^{-2}\ yr^{-1}$ *(0-1cm depth interval)*. *Reduction in the atomic C/N values combined with analysis of sedimentary pigments indicates an upcore shift from macrophyte grasses to algae, which included cryptophytes. Evidence suggests Dove Sound is undergoing eutrophication from an increase in nutrient supply and/or increase in water column residence time. This affects autochthonous productivity with shifts in primary producer abundance. This study does not support previous studies indicating septic wastes as the common nutrient source*

Introduction:

Like many coastal areas in the world, the State of Florida (USA) has undergone extensive infrastructure development during the last century to accommodate an increase in annual residents as well as millions of seasonal visitors (Hirtz and Cecil 2008). Associated with managing economic growth are environmental changes attributed to these residential, commercial and industrial developments. Pollution and land-use issues regarding commercial scale agriculture and fertilizer dispersion, solid waste disposal and potable water usage contribute to nutrient runoff which can lead to increased potential for coastal eutrophication (Turner *et al.* 2006; Gray 1982). Nutrients may originate elsewhere and be transported to coastal areas through multiple vectors such as atmospheric, long or near shore currents or channeled within sub-surface carbonate facies specific to Florida (Corbett *et al.* 1999). This complexity compounds identification, management and mitigation practices regarding coastal eutrophication processes (Davis *et al.* 1992; Gibson *et al.* 2008; Livingston 2001).

During initial phases of residential development among the islands within the Florida Keys, grey water and residential solid wastes were discharged into septic wells that had been excavated in the surficial soil and karstic structures (1-3m depths) resulting in an estimated 10,000 unregulated cesspits (U.S. EPA 1996). These disposal systems leached wastes into the upper (3m) of the limestone, flowing directly to nearby basins, causing potential risks to human health and impacting aquatic systems (Paul *et al.* 1995a:

Risk *et al.* 2009). Beginning in the 1970s larger capacity septic wells were drilled deeper (10+ m) into the limestone facies resulting in an estimated 30,000 onsite disposal system (OSDS).

The regulated OSDS wells were often unlined, still allowing seepage of the septic waste material throughout the depth of the well column. Combined with cesspit inputs, OSDSs are contributing over 550 kg N day^{-1} (U.S. EPA 1996). These localized point source wastes are then subject to transport from one island to the next (Corcoran 2006). To better mitigate the effluent from the larger developments (i.e., hotels/motels/condos), a process of deep well injection (up to 28m) was used to transport septic wastes deeper underground, and subsequently transporting materials further offshore (4 miles near Key Largo), (Shinn 1988). As canals were cut into the limestone bedrock to provide boating access, hydrologic gradients were compromised affecting the primary offshore transport of the injection wells (Paul *et al.* 1997).

Identifying and quantifying potential nutrient fluxes are necessary in order to evaluate anthropogenic impacts on coastal aquatic environmental systems (Lapointe *et al.* 2004) as coastal eutrophication processes are often magnified when dealing with island systems and anthropogenic pollutants (Lacerda 2004). Impacts to the natural communities of corals and mangroves along the Atlantic Coast have been observed, resulting in reductions of varied ecosystem services such as hurricane mitigation and wave buffering (Lapointe *et al.* 2004). Seagrass beds have become overgrown with algae, degrading essential marine habitat and impacting fish populations (Paul *et al.* 1997; Shinn *et al.* 1994; Davis *et al.* 1992).

The Florida Bay side of the Florida Keys has been subjected to agricultural byproducts in the form of transported nutrients (3,850 ±404 ton N $year^{-1}$) (Gibson *et al.* 2008) and particulate organic material (POM), impacting both corals and seagrass (Zieman *et al.* 1999). An extensive network of canals extending from Lake Okeechobee has been associated with the transport of anthropogenic pollutions (Figure 1a) (Xu *et al.* 2010; Gibson *et al.* 2008). These structures were originally designed before the 1950s to drain the Everglades exposing the rich histosols and creating productive lands then used for large commercial farms and sugar plantations (Snyder 2004). Additional point source inputs from urbanized areas and storm-water runoff near Miami Florida that eventually flow into the Atlantic Ocean on the Northeast side of the Florida Keys (Figure 1a) (McKenzie and Irwin 1983).

It is not possible to determine historic environmental quality from current water samples because the hydrology is subject to constant change. Therefore, the ability to identify earlier (potentially pre-anthropogenic) baseline conditions as well as decadal shifts from sediment stratigraphy is an effective way to estimate environmental change (Brezonik and Engstrom 1998). Historic (150 year) anthropogenic ecosystem influences and land use changes can often be captured within the sediment record of nearby systems (Meyers and Teranes 2001; Ruiz-Fernández *et al.* 2011; Gonneea *et al.* 2004). These aquatic basins can archive stratographic deposition that may be used for identifying natural changes in trophic productivity and sedimentation rate, as well as environmental impacts associated with residential, commercial, and recreational modifications (Turner *et al.* 2006; Smoak *et al.* 1999; Waters *et al.* 2010).

While multiple nutrient studies have been conducted on Florida Bay and the local nearshore Atlantic Reef, little is known about historic nutrient influence and anthropogenic impacts on the individual Keys (Fourqurean and Zieman 1992; Xu *et al.* 2007; Lamb and Swart 2008). The Dove Sound tidal lagoon system (Figure 1b) located in Tavernier Florida (Key Largo), offers a temporal repository unique to the Upper Florida Keys by providing a potential depositional environment comprised of a natural basin surrounded by transitional mangrove ecotones that lies between Florida Bay and the nearshore reefs along the Atlantic Coast.

Dove Sound borders sites that have undergone multiple stages of development, channelization and land use alteration. Residents living around the lagoon cited anecdotal evidence suggesting these disturbances caused "a loss of fish diversity, a reduction of sea grasses and an increase in algae and mud" over the last 20 years (Personal communications, J. Grove). Historic records of anthropogenic landuse changes like highway construction and commercial development offer the potential to correlate these events with environmental impacts as recorded in the sediment record.

The degradation and preservation of organic sediments within coastal systems remains complex as marine productivity is affected by both biotic and abiotic variables which influence the isotopic signatures and occurrence of phototrophic species in depositional environments (Anderson and Fourqurean 2003; Furlong and Carpenter 1988; Lapointe *et al.* 1992). Nutrients from sources like solid waste runoff can contribute to coastal eutrophication and have been identified by isotopic enrichment (Anderson and Fourqurean 2003; Meyers and Teranes 2001).

Sediment accumulation rates for the system were established through radiometric ^{210}Pb dating and application of the Constant Rate of Supply Model (CRS) (Appleby 2001; Appleby and Oldfield 1978). Sectional core aliquots were further analyzed for total nitrogen (TN), total organic carbon (TOC), $\delta^{13}C$, $\delta^{15}N$, as well as sedimentary photosynthetic pigments as these proxies provide a means to identify sedimentary sources and process within the system. Stable isotopic values like $\delta^{15}N$ have been used to differentiate between natural or anthropogenic sources of nitrogen, while $\delta^{13}C$ has been used to differentiate type of organic carbon sources such as aquatic vs. terrestrial origins. Atomic C/N ratios in conjunction with $\delta^{13}C$ values are used as further indicators of sequestered organic material composition and potential producer origin. Higher C/N ratios are common in terrestrial plants as carbon dense structures are required for greater support while aquatic organisms often rely on buoyancy within the water column for support (Bouillon et al. 2003). Plants produce a multitude of photosynthetically derived pigments, many of which are species specific and have proven to be stable in aquatic depositional environments (Qian *et al.* 1996; Kowalewska 2005). Determination of indicator groupings such as diatoms, algae and cryptophytes as well as and secondary degradation products (Chlorophyll a to Pheophytin a) provide evidence of individual species occurrence. These deposited proxies have been utilized to indicate nutrient fluxes, trophic shifts, system alterations and eutrophication as a result of anthropogenic pollution (Schottler and Engstrom 2006).

The goal of this research is to establish a historic 100yr time-scale baseline condition, provide a timeline for potential changes in sedimentation rates, determine composition of deposited materials and identify shifts in trophic producer communities.

This environmental datum will provide information for managers, engineers and citizenry who may need to address issues of sustainability and remediation in order to support existing communities and design future developments within the Florida Keys (Smol 1992; Dewitt *et al.* 2004). The working hypothesis of this research is that local infrastructure improvements, specifically the recent expansion and fortification of US Highway 1 during the 1960s and 1970s (Figure 1b), led to a hydrological change by impounding the natural Bay to Atlantic flow of the system. Additionally, this system has potentially been affected by the historical nutrient loading associated with localized septic system leachates. Lagoonal sediments will be used to examine influence of anthropogenic nutrient fluxes, increased system productivity, sedimentation rates and potential delivery vectors leading to system eutrophication (Smoak and Swarzenski 2004; Ellison 2008).

Site Description:

Dove Sound (Figure 1b) is a shallow (4m depth / 0.09km^2 total surface area) lagoon located near Key Largo in the Upper Florida Keys. It is tidally dominated, mean tidal range 1m (Corbett *et al.* 1999) by a single natural creek (3m depth / 1km length) that connects it to the Atlantic Ocean to the East. The surrounding highlands are defined by rocky hummock with transitional areas of mangrove swamp which border the entire system. Two “borrow pits”, Blue Water Borrow Pit (1990s) and Redlands Borrow Pit (1970s) (Figure 1b), were excavated and the quarried limestone materials used for an 18 mile expansion and fortification of nearby US Highway 1. This roadway which runs north to south linking the many islands that comprise the Florida Keys ecoregion, was built after the 1935 Labor Day Hurricane to replace the damaged railway. There are two distinct developments present, Harris Ocean Park Estates and Dove Creek Estates that were developed in 1950 and 1960) respectively. Dove Creek Estates lies 0.5 km (midpoint) along Dove Creek (Figure 1b) with artificial canals providing boating access to the Atlantic coast and into Dove Sound (limited access). Harry Harris Park (Monroe County Park) lies at the north-eastern end of Harris Ocean Park Estates and contains a recreational grass baseball field.

Methodology:

In December 2010, a sediment core was collected from within the Dove Sound basin (25°01’38.2”N, 80°30’05.7”W) utilizing a 10cm diameter, clear polycarbonate sampling tube inserted at the sediment-water interface to an approximate 50cm sediment depth. The core was capped to reduce any disturbance to the flocculent sediment interface before extraction from the seabed (Glew *et al.* 2001). During collection, transport and storage, care was taken to minimize disturbance of the sediments. To reduce the degradation of the pigments, the core was wrapped with dark material and stored vertically in a cold room until processed (Leavitt and Hodgson 2001).

The sediment core was vertically extruded and sliced at 1cm intervals for the top 10cm of the core with the remainder being sectioned into 2cm intervals. A volumetric aliquot of each interval was dried at 105°C for 24 hours to determine dry bulk density (g dry cm^{-3}wet) and then combusted at 550°C for 1hour to determine percent organic matter (LOI). A portion of each section was freeze-dried, then ground into a powder and packed into gamma tubes and sealed with epoxy. Sealed sample tubes were stored for at least 21 days to allow the in-growth of the ^{222}Rn daughter product (Appleby 2001). After secular equilibration was reached, the samples were placed into the well of an intrinsic germanium detector coupled to a multichannel analyzer. Initial ^{210}Pb activity was determined by direct measurement of the 46.5KeV gamma peak and ^{226}Ra was measured via its decay product ^{214}Pb, at the 351.9KeV gamma peak. Measured counts per minute were converted to disintegration per minute (dpm) based on a factor determined from standard calibration. Self-absorption coefficients for a relatively low mass (e.g. 1.5 g) have been determined to be within a few percent of material used for standard calibration, make self-absorption corrections unnecessary (unpublished data). Unsupported activity is calculated by subtracting the ^{226}Ra activity (as measured by the ^{214}Pb) from total ^{210}Pb activity. Unsupported (excess) ^{210}Pb values are determined for each sectioned layer providing an unsupported ^{210}Pb inventory for the core. Errors are determined based on standard counting errors propagated along with standard counting errors for standards and backgrounds (Smoak *et al.* 2000). The CRS model was used to quantify deposition rates and to calculate nutrient fluxes over the last 100 years (Appleby and Oldfield 1978).

Photosynthetic pigments were measured using an HPLC system following the methods of Leavitt & Hodgson (2001) designed specifically for sedimentary pigments. Pigment samples were extracted from the sediment with a solvent mixture of acetone, methanol and water mixed in an 80:15:5 ratios, which contained an internal standard (Sudan II; Sigma Chemical Corp., St. Louis, MO, U.S.A.) and allowed to digest 16–24 hr in a 20 C° freezer. Following extraction, samples were centrifuged and filtered through a 0.22µm syringe filter to remove any particulate matter from the sample. Samples were placed in an auto-sampler tray where they were mixed with an ion-pairing agent (0.75 g tetrabutylammonium acetate and 7.7 g ammonium acetate in 100 mL HPLC-grade water) prior to injection. A Shimadzu HPLC system injected 200 µL of each sample following the mobile phase and time sequence method of Leavitt & Hodgson (2001). Chlorophylls and carotenoids were separated by passing through a Rainin Model 200 Microsorb C18 column and measured using a photodiode array detector set at 435 and 665 nm. Pigments were identified using retention times of known standards and pigment specific spectra recorded by the detector. Pigment concentrations were expressed as nmol $g^{-1}$of dry organic matter, and calculated by comparing peak areas against standards of known concentration. Primary producer group affinities with the different pigments analyzed were based on known associations (Leavitt & Hodgson 2001) and measured macrophyte material from Dove Sound. Zeaxanthin and lutein are reported together due to extraction process.

Stable isotope samples were analyzed with a Delta Plus XP mass spectrometer interface with a Carlo Erba Elemental Analyzer. Samples were combusted at 1020ºC. Before measurement, the samples were treated to remove inorganic C (HCl fumigation technique) and then wrapped into tin capsules. Samples were run in duplicates with the analytical errors based on long-term standard analyses and are better than 0.3 (1 standard deviation) for N and C isotopic ratios, better than 8% (1 relative SD) for N% and C% (Harris *et al.* 2001).

Results:

Data sets were divided into two specific groups; dated and non-dated. The dated portion included the top 12 cm. The non-dated portion was from 12-20cm depth (total of 4 sections) representing the pre-1878 depositional environment and determined for use as the baseline conditions. The total unsupported ^{210}Pb inventory calculated for the DS2S core was 9.72±0.22 dpm cm^{-2} which represents an approximate 130 year chronologic horizon. Mass sedimentation rates increased upcore approximately 10 fold from 5.0 ±0.97 mg cm^{-2} yr^{-1} (10-12cm depth interval) to 48.58±3.61 mg cm^{-2} yr^{-1} (0-1cm depth interval) (Table 1 / Figures 2 and 3).

Dry bulk densities (g dry cm^{-3} wet) transitioned upcore from an average 0.36±0.12 (12-20cm) to 0.15±0.04 (0-12cm) (Table 1). Nutrient analysis indicated that both sedimentary total organic carbon (TOC) and total nitrogen (TN) concentrations increased over the last 130 years (Table 1 / Figure 4, 5). The C/N atomic ratio transitioned from an average of 21.31±2.34 (12-20cm) to an upcore average of 13.72±1.22 (0-12cm). The mass percentage of TN increased from 0.46±0.08% (12-20cm) to 1.32±0.20% (0-12cm). The average percent TOC transitioned from 8.47±2.50% to 15.41±1.99% respectively. The $\delta^{15}N$ values decreased upcore from 1.17±0.16 (12-20cm) to 0.43±0.29 (0-12cm). This value decreased below assumed atmospheric ratio (0.00‰) into a slightly negative range of -0.02 in the 9-10cm (1923-1953) section. The $\delta^{13}C$ values varied little over the 20cm depth averaging -21.77 ±0.67‰ (Figure 6).

Sedimentary pigment analysis indicated an increasing upcore depositional trend of diatom indicators (fucoxanthin & diatoxanthin), cyanobacteria indicators (myxoxanthophyll, echinenone, canthaxathin, and zeaxanthin-lutein) as well as chlorophylls a, b and β-carotenes (Table 2, Figure 7). In the 12-20cm depth sectioned intervals, pigment abundance was relatively stable with many values below detectable levels. Upcore values (0-10cm intervals) reflected relatively greater deposition and increased species occurrences beginning in the 1920s. Cryptophytic algae pigment values (alloxanthin) transitioned from below detection levels (≤0.00nmol g^{-1}) within the 12-20cm intervals to > 2.20 nmol gr^{-1} starting in the 1990s

Discussion:

The Dove Sound system exhibits an upcore trend of increasing mass sediment accumulation, TOC and TN (Figure 2, 4 and 5). Depositional flux may be the result of: alterations to the hydrology affecting the flow of material in and out of the lagoon or water column residence time, landuse changes influencing upland runoff, increase source of nutrients resulting in additional productivity, or a combination of variables. Depositional changes associated with landuse alteration and the increased transport of upland material could potentially increase mass accumulation as additional organic materials are contributing to sediment load. A reduction in flow of material out of the system or increased residence times also would contribute to the sediment load.

The unsupported Pb-210 inventory for the DS2S core of 9.72±0.22 dpm cm^{-2} is a slightly lower value than determined by Settle et al. (1982) in Florida Bay of 14.19 dpm cm^{-2} (calculated from annual flux rate). This difference may be attributed to less atmospheric supply and/or system export of sediment materials (Appleby and Oldfield 1978). If Dove Sound was experiencing deposition flux associated with the increased transport of material from landuse alterations the ^{210}Pb inventory should reflect an increase (Figure 3) as the deposition of transported upland materials would be contributing additional atmospheric ^{210}Pb. Therefore the lower inventory indicates that sediment focusing is not an important process in this system (Crusius and Anderson 1995; Robbins *et al.* 2000). In addition if upland areas were supplying more materials the $\delta^{13}C$ would be expected to shift to more negative and C/N atomic ratios would increase, which is the opposite of what is observed (Peterson and Fry 1987). Therefore increased contributions from upland materials do not seem to be likely as the explanation for the upcore depositional flux.

If a reduction in the tidal flushing or mean flow was occurring in Dove Sound, hydrologic export of materials should be reduced, resulting in increasing contributions of the same type of sediments over time. However, beginning in the 1920s, both the %TN and %OC of the sediments increased upcore (Figures 4, 5) (Table 1) as the C/N atomic ratio decreased indicating a shift in the composition of sediment material from the pre-1878 (12-20cm depth) environment. This depositional trend continues upcore for the next 90 years (Figure 2) with C and N mass accumulation increasing as the C/N atomic ratio decreased to 12.53 (1-2cm) indicating a shift in primary depositional materials.

Isotopically, the local marine systems within Florida Bay, exhibit $\delta^{13}C$ variability from mangroves (*Rhizophora mangle)* ranging from -35 to -22‰: avg -27‰) (Fry and Smith 2002), bulk sediments -16.2 to -9.6‰ and epiphytes -16.7 to -11.0‰ (Williams *et al.* 2009) to sea-grass (*Thalassia testudinum)* ranging from -24 to -3‰: avg -22‰ (Hemming and Mateo 1996). When the lower C/N values are plotted in relation to the overall record of $\delta^{13}C$ values of -21.77‰ ±0.67‰ (0-20cm) for Dove Sound (Figure 8), the historic $\delta^{13}C$ vs. C/N relationship indicates a shift in carbon source similar to flora such as macrophyte grasses with C/N around 16.49±0.09‰ (Fourqurean and Zieman 1992) and nearshore marine algae that can range from 11.5 to 16.3‰ depending on dominant species (Lapointe et al. 1992).

This evidence indicates that sediments are not the result of runoff from upland areas as the $\delta^{13}C$ would be more negative and C/N values would be more indicative of terrestrial species. Despite the proximity of the mangroves within the system the mangrove litter is not a discernable source of organic material in the sediment stratigraphy (Kristensen *et al.* 2008). A more negative $\delta^{13}C$ value would be expected (closer to -27‰) if mangrove detritus were being sequestered as tidal export was reduced (Fry and Smith 2002). The $\delta^{13}C$ values for Dove Sound are within the lower range for mangroves but are more representative of seagrass and marine algaes (Boulion *et al.* 2003). The sequestered carbon throughout the core is more representative of marine aquatic productivity (Meyers 1994; Muzuka and Shunula 2006).

Increased residence times of water bodies can also alter the isotopic signature as nutrients are recycled (Muzuka and Shunula 2006; Walter *et al.* 2007). Shifts in isotopic values ($\delta^{13}C$ & $\delta^{15}N$) associated with internal loading are often difficult to determine as they are subject to multiple variables (temp, oxic vs. anoxic, degrader, DIN source) but have been estimated to be as much as +3‰ (Lehmann et al. 2002). While Dove Sound has undergone enrichment in both the $\delta^{13}C$ and $\delta^{15}N$ values, these minimal shifts might be associated with depositional variation in contributions from trophic producer type (e.g. seagrass vs. algae) (Muzuka and Shunula 2006). This shift is dependent on the contributional flux of $\delta^{13}C$ value from the dominant depositional material (Osterman *et al.* 2005). The potential for increased residence times and associated internal nutrient loading within Dove Sound can not entirely be discounted. Based on the upcore shifts in percent OC and TN, C/N values, mass accumulation of both C and N, and $\delta^{13}C$ and $\delta^{15}N$ the increasing sedimentation tend is the product of system eutrophication resulting in increased trophic productivity and not an increase of material transport or impoundment.

However, the relative contribution from external loading versus internal cycling of nutrient supply cannot be determined.

Quantifying producer abundance through time can be used to interpret ecological conditions to include nutrient related trophic shifts and geochemical changes associated with land use alterations (Sanders *et al.* 2010*;* Xu *et al.* 2007). Trophic producer community analysis based on sedimentary pigments (Table 2 and figure 6) indicates a low nutrient initial condition within the seagrass beds that shifts upcore. Deeper core material was representative of a limited nutrient benthic system of macrophyte grasses as the pre-1878 average values of $\delta^{13}C$ were -21.77 ±0.67 with a C/N ratio of 21.31±2.34 (Lapointe *et al.* 1992). This was followed by a trophic transition during the 1920s to increased epiphytic algae as C/N values began decreasing to 14 while the $\delta^{13}C$ values remained relatively stable, indicating continued marine source of organic carbon (Table 1, 2 / Figure 7, 8).

Diatoms, Cyanobacteria and β-carotene indicator pigments increased their depositional concentrations threefold, maintaining even higher values upcore. During this same time period alloxanthins, which were below detection levels in the pre-1878 sections, increased in deposition abundance reaching an upper core value of 3.59 nmol g^{-1} org. This specific pigment is indicative of cryptophytes which are motile within the water column (Leavitt and Hodgson 2001). This family is an indicator of eutrophication and is common in algal blooms which can interfere with light transmission within the water column contributing to anoxic conditions and affecting benthic organism like sea grasses (Personal communications, M. Waters). Increasing occurrence of these biomarker pigments (zeaxanthin/lutein complex, alloxanthin, β-carotene) within the sediment stratigraphy indicates an increasing advantage for algal over macrophyte dominance within the Dove Sound system. Increasing nutrient derived productivity causing shifts in trophic producer abundance also agrees with the reductions of the C/N values as well as depositional trends of increasing mass accumulation of N and C within the sediments.

During this trophic producer shift, the $\delta^{15}N$ values decreased indicating a potential alternative source of available nitrogen being added to the system thereby supporting the algal dominance and resulting system eutrophication. Eutrophication is common in coastal waters as runoff from land transports nitrogen and other nutrient materials that support phototrophs and has been linked to harmful algal blooms (HAB) affecting fisheries, aquatic health and humans (Armitage *et al.* 2005: Nixon 1995; Paul *et al.* 1995b). Delta ^{15}N values higher than natural atmospheric deposition of nitrogen (0.00 ‰) are common within a septic (>3.0‰) nutrient affected system as the ^{15}N is bio-accumulated and biomagnified through the trophic levels (Lapointe *et al.* 2004). Delta ^{15}N values can also be elevated when high levels are introduced by humans into local systems through solid waste practices. Higher $\delta^{15}N$ values can also occur within sediments as decomposers tend to select the lighter ^{14}N, thereby enriching sediments with the heavier isotope and increasing the $\delta^{15}N$ values (Meyers *et al.* 2001; Gearing *et al.* 1991; Meyers 1994).

Previous studies indicating that septic wastes are a primary influence of anthropogenic pollution and a leading cause of eutrophication in the Keys (Paul *et al.* 1997; Gearing *et al.* 1991; Lapointe *et al.* 2004) are not supported within Dove Sound. The $\delta^{15}N$ values are relatively low (Table 2 / Figure 5) and are closer to normal atmospheric nitrogen cycle $\delta^{15}N$ ratios that range -2‰ to 2‰: with 0‰ as assumed atmospheric (Peterson and Fry 1987; Meyers and Teranes 2001). The nearby septic well tracer studies (Paul *et al.* 1995a), looked at canals that cut into the limestone facies, disturbing the karstic stratification that supports pressure gradients for groundwater flow that transports wastes offshore. If this was also the case in Dove Sound, the septic wells in the Dove Creek Estates Subdivision development along Dove Creek should be contributing TN with higher $\delta^{15}N$ values in the waters being tidally transported into the system, providing these nutrients for increasing productivity. This is not the case as shown by the historic $\delta^{15}N$ record and the lack of a more positive $^{15}N/^{14}N$ relationship ranging from 3‰ and up for septic wastes (Lapointe *et al.*1990; Meyers and Teranes 2001).

The upcore concentration of TN within the lagoon has increased from 0.46±0.08% (12-20cm) to 1.32±0.20% (0-12cm), however, the $\delta^{15}N$ values have shifted from 1.17±0.16 average baseline levels in the pre-anthropogenic 12-20cm sections to being isotopically lighter 0.43±0.29 (average over dated range 0-12cm). These lower $\delta^{15}N$ findings usurp previous impact studies and potentially indicate runoff from synthetic fertilizers or internal cycling as the anthropogenically altered nutrient source for the system (Heaton 1986). The Haber-Bosh technique produces agricultural fertilizers that are rich in NH_3 and express $\delta^{15}N$ values close to atmospheric (Meyers 2001). Dispersion of this material has been shown to greatly accelerate phototrophic productivity and subsequent deposition of TON in coastal systems (Holland *et al.* 1999). Historic flux to Dove Sound from this type of source would account for the lower $\delta^{15}N$ (near 0.00‰ atmospheric ratio), as well as account for the increased productivity and subsequent eutrophication trend. Direct determinations for point sources of this anthropogenic material remain uncertain; however vectors for delivery may be limited to the sediment / bedrock unconformity (Shinn *et al.* 1994). Florida Bay ground water studies using radiometric tracers express higher $\delta^{15}N$ values, closer to 5‰ (Corbett *et al.* 1999). If these waters were acting as a vector then the higher $\delta^{15}N$ would have contributed ^{15}N enrichment to sediment levels, which was not detected in the Dove Sound core.

Flow captured within the subterraneous karstic stratification from Florida Bay expresses a general hydrologic pressure gradient greater than that of the Atlantic (Shinn *et al.* 1994). This pressure induces positive tidal pumping and hydrologic flow from Florida Bay on the West side of Dove Sound through the key to the nearshore Atlantic Coastal areas on the east side. This mechanism explains both the transport of the nutrients being carried within Florida Bay into Dove Sound, but also the local septic wastes being kept out. Tidal studies on annual mean flow have been conducted on Tavernier Creek indicate a general minimal net flow from Florida Bay to the nearshore Atlantic (Smith 2005). Florida Bay is acting as a carrier for these nutrients (Gibson *et al.* 2008) and they are being deposited in Dove Lake through tidal pumping and surficial aquifer exchange.

Harry Harris Park and other areas (Figure 1b) could be contributing isotopically lighter nitrogen from the fertilization of their recreational areas to the flux being transported into the lagoon. However, this material would be working against this hydrologic gradient and should also potentially be carrying septic wastes back into the lagoon either from runoff into the Atlantic and traveling tidally back up Dove Creek or within the subsurface unconformities which would also cross Harris Ocean Park Estates, which is not supported by the isotopic evidence.

Conclusion:

The Dove Sound system has been impacted by changes in the nutrient concentrations of available nitrogen in Florida Bay associated with agricultural run-off and / or increased residence times causing eutrophication (Nixon 1995; Voss *et al.* 2000). The flux of dissolved nitrogen to the system supported an increase in organic productivity and a shift in the historic primary producer community. This process involved an increase in the algal community relative to the original seagrass beds. These autochthonus organic sediments are deposited and sequestered as a result of increasing nutrients being introduced into the system via tidal pumping of the surficial aquifer flow and/or internal nutrient cycling and not from local land-use changes or marine access channelization. This is supported by the $\delta^{13}C$ ratio and C/N values which do not indicate an increase in depositional material being derived from the surrounding mangrove vegetation.

While a contribution from fertilizer pollution is suspected, direct determination of this nutrient source has not been linked in Dove Sound. Fertilizer runoff has been associated with eutrophication in Florida bay and to nearshore coral reef structures and increases in occurrence and duration of harmful algal blooms (Lapointe *et al.* 2004). Septic sources of nutrients were not supported as the $\delta^{15}N$ values were below established indicator levels (Lapointe *et al.* 1990; Shinn *et al.* 1994). Any restoration efforts in Dove Sound will need to further investigate the relative contribution of nutrients from Florida Bay and the influence of increased water column residence times on eutrophication.

Tables:

Table 1: CRS Model Dating Profile / Stable Isotope Data:

Sample Depths (cm)	Model Date Range	Mass Sedimentation Rate (mg cm^{-2} yr^{-1})	$\delta^{15}N_{air}$ ‰	$\delta^{13}C_{PDB}$ ‰	N%	C%	C/N Atomic Ratio	Dry Bulk Density (g-dry/cc wet)
0-1	2010-2008±1	48.58 ± 3.61	0.61	-21.91	1.19	12.80	12.53	0.11
1-2	2008–2005±1	32.93 ± 3.25	0.65	-22.16	1.35	14.56	12.61	0.11
2-3	2005-2002±1	32.59 ± 1.94	0.74	-22.12	1.33	14.63	12.81	0.10
3-4	2002-1997±1	29.14 ± 2.60	0.60	-21.92	1.51	16.52	12.79	0.12
4-5	1997-1993±1	29.0 4± 2.12	0.44	-22.01	1.55	17.16	12.94	0.14
5-6	1993-1988±1	26.12 ± 1.68	0.38	-22.13	1.53	17.31	13.18	0.13
6-7	1988-1981±1	22.71 ± 1.63	0.11	-22.21	1.35	15.97	13.84	0.14
7-8	1981-1970±1	15.78 ± 0.93	0.18	-22.10	1.33	15.75	13.87	0.18
8-9	1970-1953±2	12.0 ± 0.94	0.20	-22.34	1.39	18.56	15.53	0.20
9-10	1953-1923±3	6.772 ± 0.72	-0.02	-21.99	1.13	14.39	14.81	0.21
10-12*	1923-1878±10	5.01 ± 0.97	0.88	-21.95	0.87	11.89	16.00	0.23
12-14	12-14cm		*1.04*	*-21.39*	*0.45*	*8.09*	*20.83*	*0.26*
14-16	14-16 cm		*1.05*	*-20.11*	*0.39*	*6.34*	*19.31*	*0.35*
16-18	16-18 cm		*1.21*	*-21.83*	*0.57*	*12.06*	*24.68*	*0.54*
18-20	18-20 cm		*1.38*	*-20.31*	*0.42*	*7.38*	*20.41*	*0.31*

**Note 2 cm intervals from 10 to 20 cm depths. Maintaining a minimal first order error of correlated age to ≤11% upcore, the dates beyond this range are considered "too old" as the propagation of errors exceeds acceptable values (Binford 1990).*

Table 2: Pigment Analysis Data Values:

	Diatoms		**Cryptophytes**	**Cyanobacteria**				**Indicators for productivity (pheo's for chl breakdown)**				**Productivity proxy**
Date Range	**fuco**	**diato**	**allo**	**zea-lut**	**myxo**	**ech**	**canth**	**chl-b**	**pheo-b**	**chl-a**	**pheo-a**	**B-car**
2010 - 2008	62.9	18.6	3.6	35.5	3.6	0.2	3.1	16.0	1.5	193.5	70.0	163.5
2008 - 2005	42.3	13.8	2.6	25.3	2.3	0.1	2.3	13.0	1.2	135.9	51.2	115.8
2005 - 2002	34.4	11.9	2.3	22.1	1.8	0.1	2.0	11.4	1.0	110.7	42.1	98.9
2002 - 1997	37.7	14.6	2.6	28.3	2.7	0.1	2.7	9.4	1.0	118.3	52.4	125.7
1997 - 1993	25.7	12.8	2.2	27.5	2.2	0.1	2.6	7.1	0.7	97.0	48.8	124.4
1993 - 1988	17.5	8.8	1.1	19.6	1.2	0.1	1.8	5.5	0.7	84.6	40.2	100.1
1988 - 1981	13.8	8.2	0.7	18.8	1.1	0.1	1.6	4.8	0.6	75.7	38.7	92.8
1981 - 1970	10.6	8.0	0.5	17.2	1.1	0.1	1.5	6.0	0.6	65.7	45.0	102.1
1970 - 1953	5.0	8.2	0.3	25.6	1.1	0.1	1.9	6.3	0.7	55.4	54.0	110.1
1953 - 1923	5.7	10.8	0.2	35.2	1.3	0.1	1.9	9.5	1.0	68.9	73.2	157.4
1923 - 1878	2.4	3.6	0.0	10.8	0.3	0.1	0.6	4.4	0.5	21.7	24.5	53.5
12-14cm	*1.2*	*1.3*	*0.0*	*3.7*	*0.1*	*0.0*	*0.2*	*1.3*	*0.1*	*7.2*	*6.9*	*18.4*
14-16 cm	*0.3*	*1.3*	*0.0*	*4.2*	*0.1*	*0.0*	*0.2*	*1.8*	*0.1*	*5.9*	*8.7*	*22.5*
16-18 cm	*0.1*	*0.6*	*0.0*	*2.7*	*0.3*	*0.0*	*0.2*	*3.2*	*0.0*	*7.4*	*6.4*	*18.8*
18-20 cm	*0.0*	*0.2*	*0.0*	*0.7*	*0.0*	*0.0*	*0.1*	*0.4*	*0.0*	*2.5*	*2.6*	*5.2*

* (nmol g^{-1} of organic material): pigments are grouped into general categories of indicator species.

Figures:

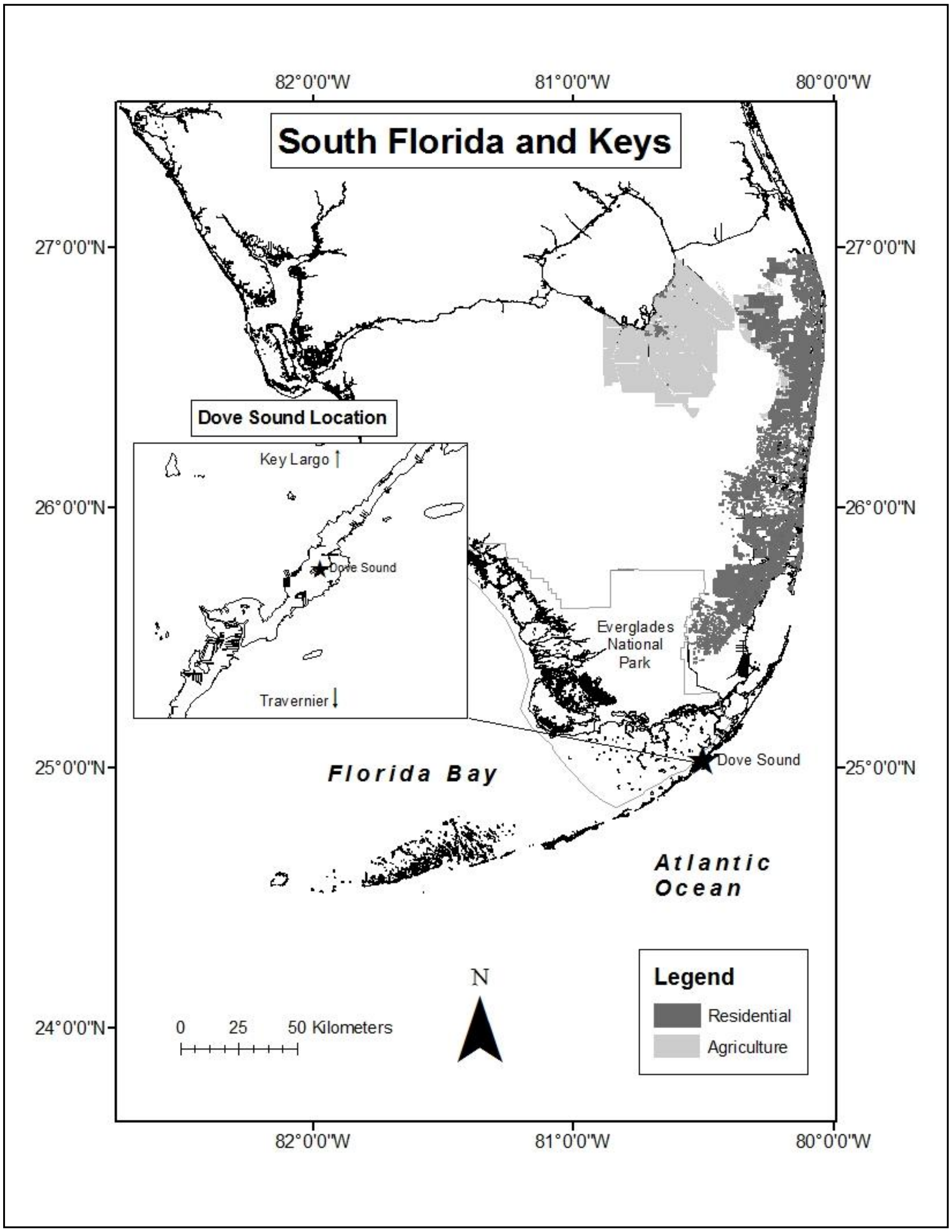

Figure 1a: Dove Sound, Tavernier Florida: Located Upper Florida Keys, USA. Greater Miami Area lies to the North East while the Everglades National Park and Agricultural areas lie to the North-northwest.

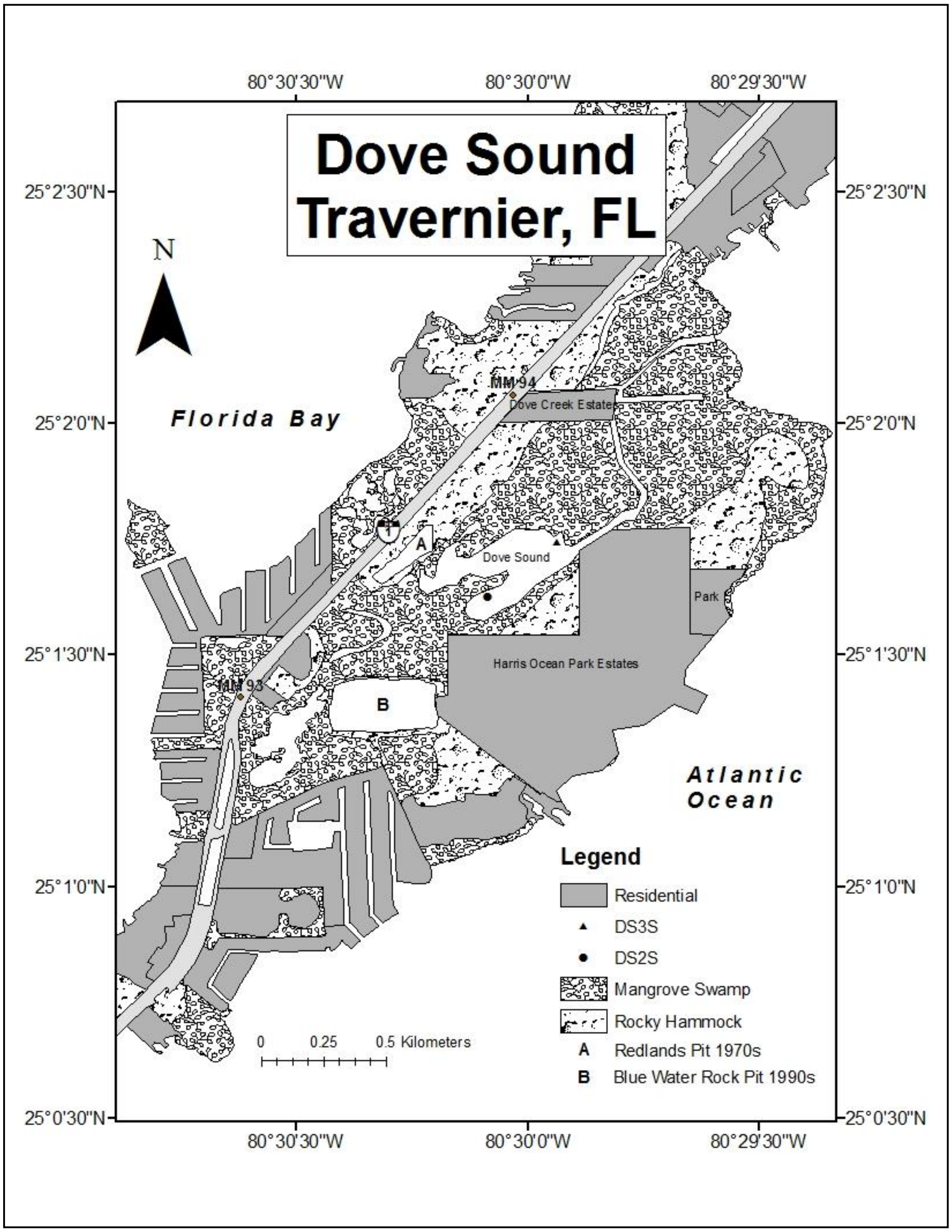

Figure 1b: Dove Sound and Dove Creek: surrounding developments and topography: *Dove Creek Estates* (Circa 1960), lies along (approx ½ way point) *Dove Creek* which is the primary tidal connection (1km linear length) / *Harris Ocean Park Estates* lies to the East (circa 1950). *Redland's Borrow pit* (est.15m depth) lies to the West (circa 1970), and Blue Water Rock borrow pit lies to the South (circa 1992).

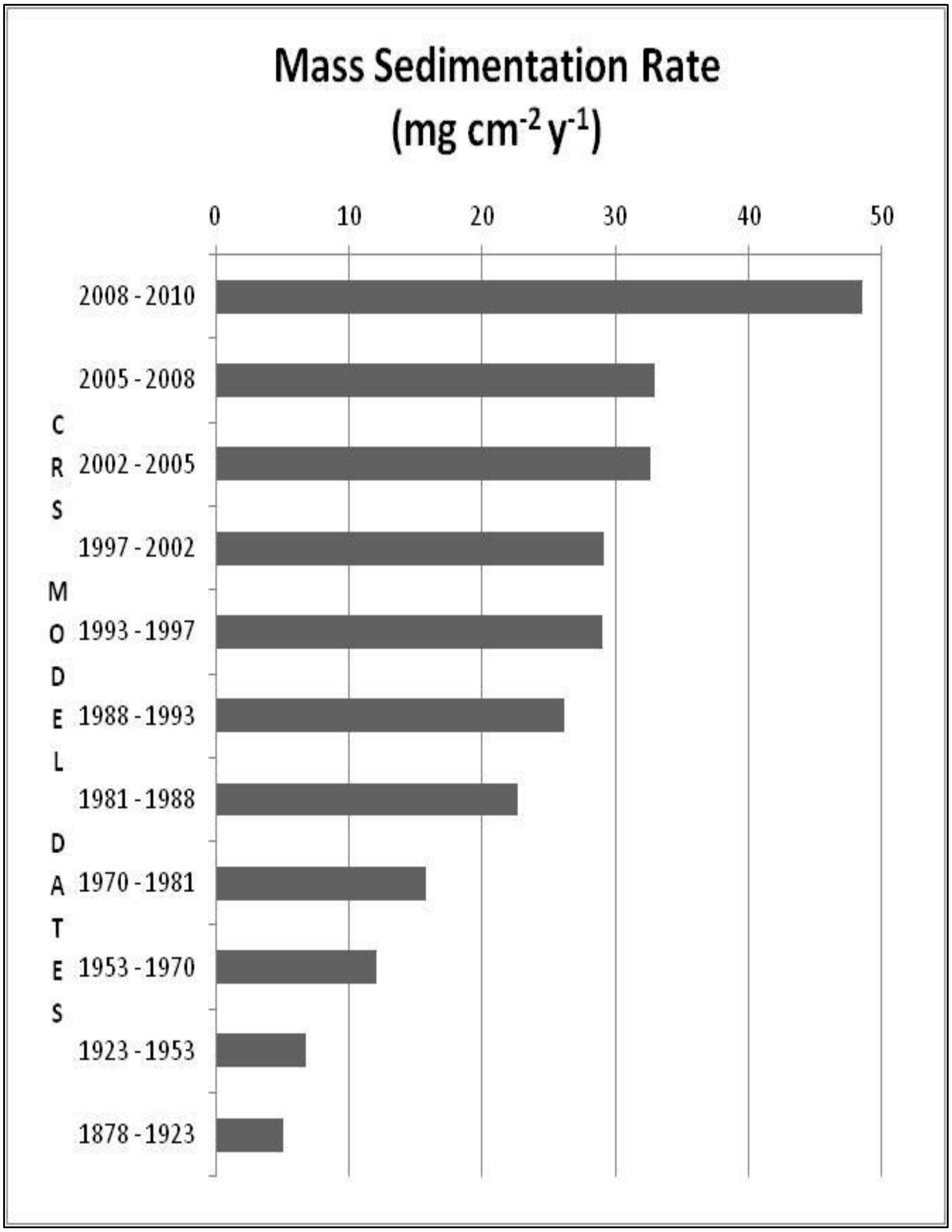

Figure 2: CRS Model Dates & Mass Sedimentation Rate:

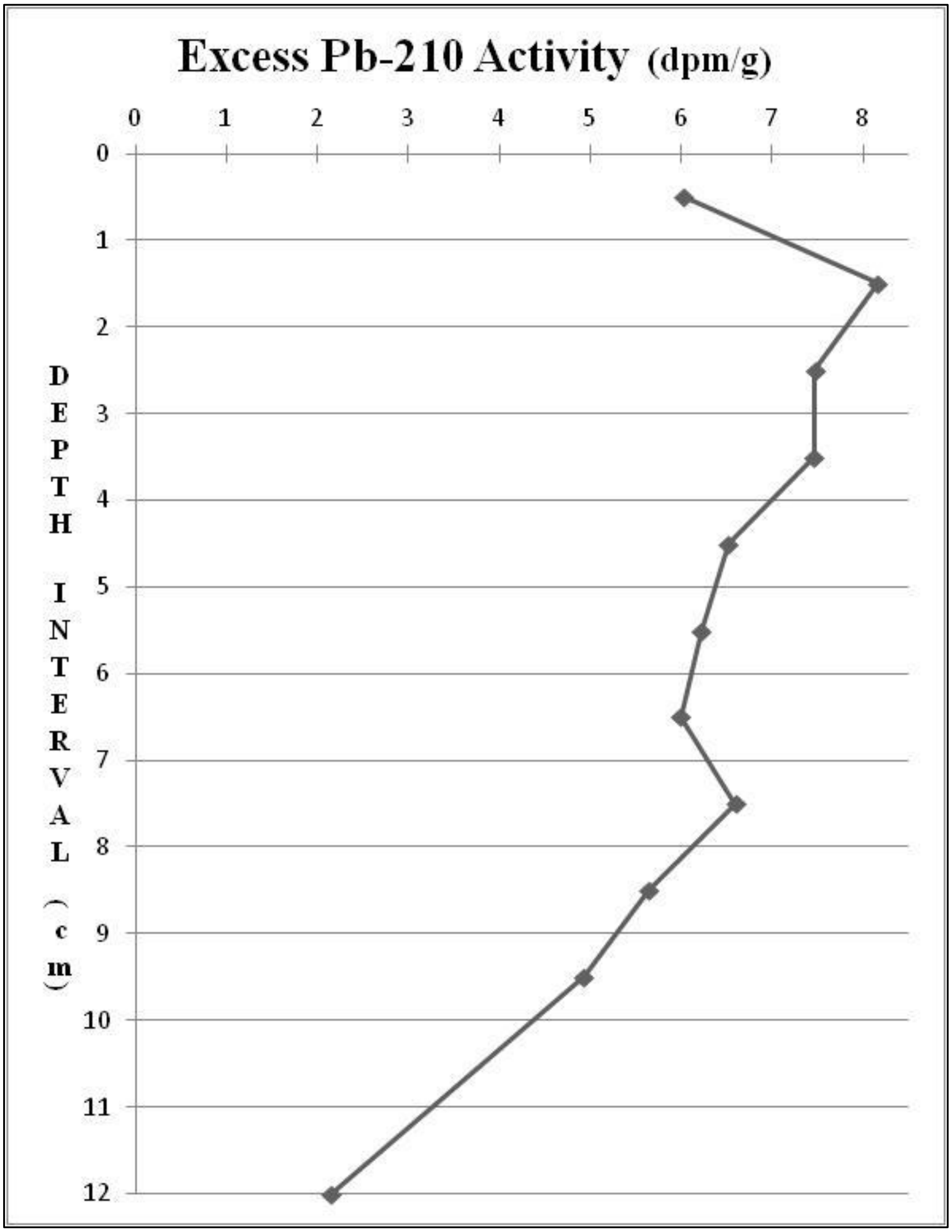

Figure 3: Lead-210 Activity vs. Depth:

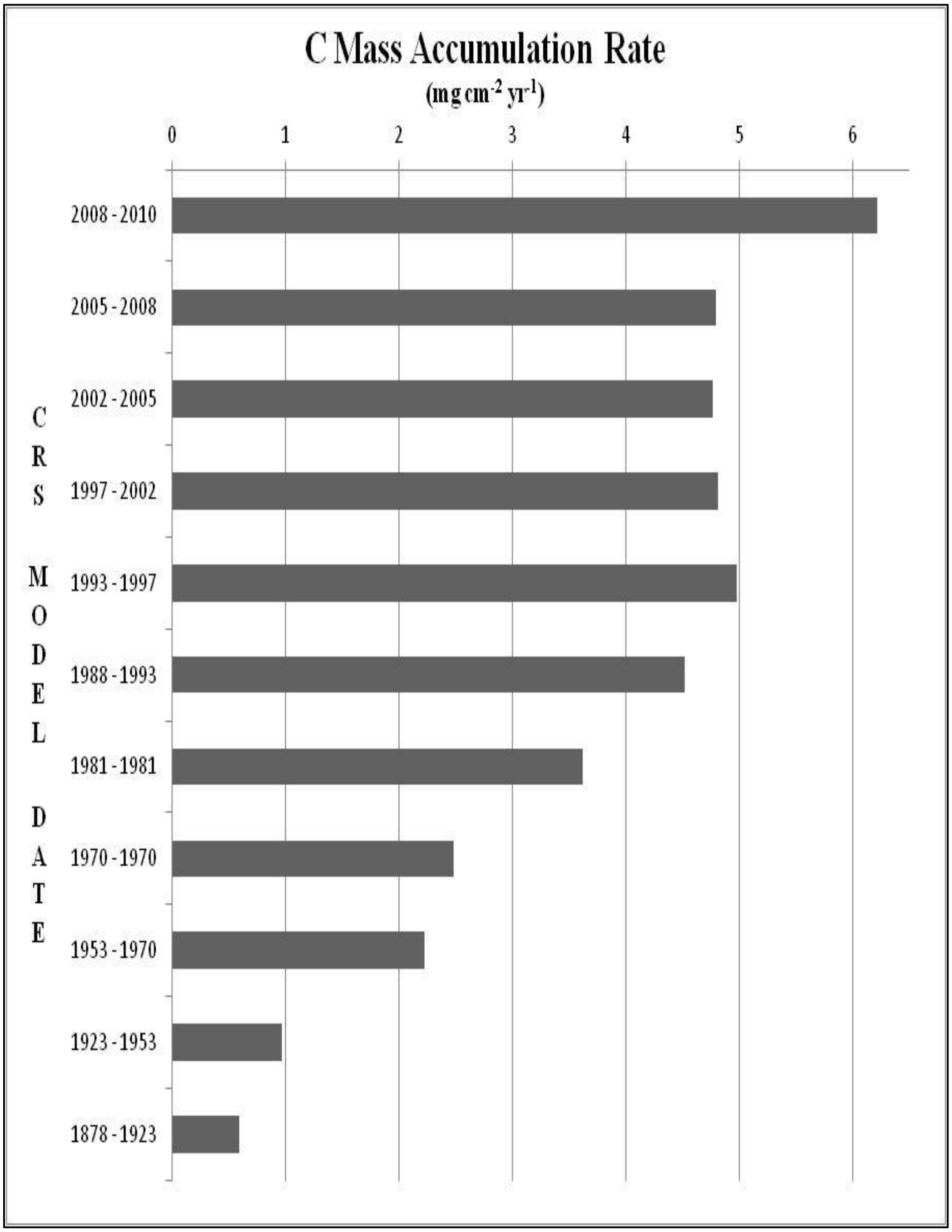

Figure 4: Carbon Mass Accumulation Rates:

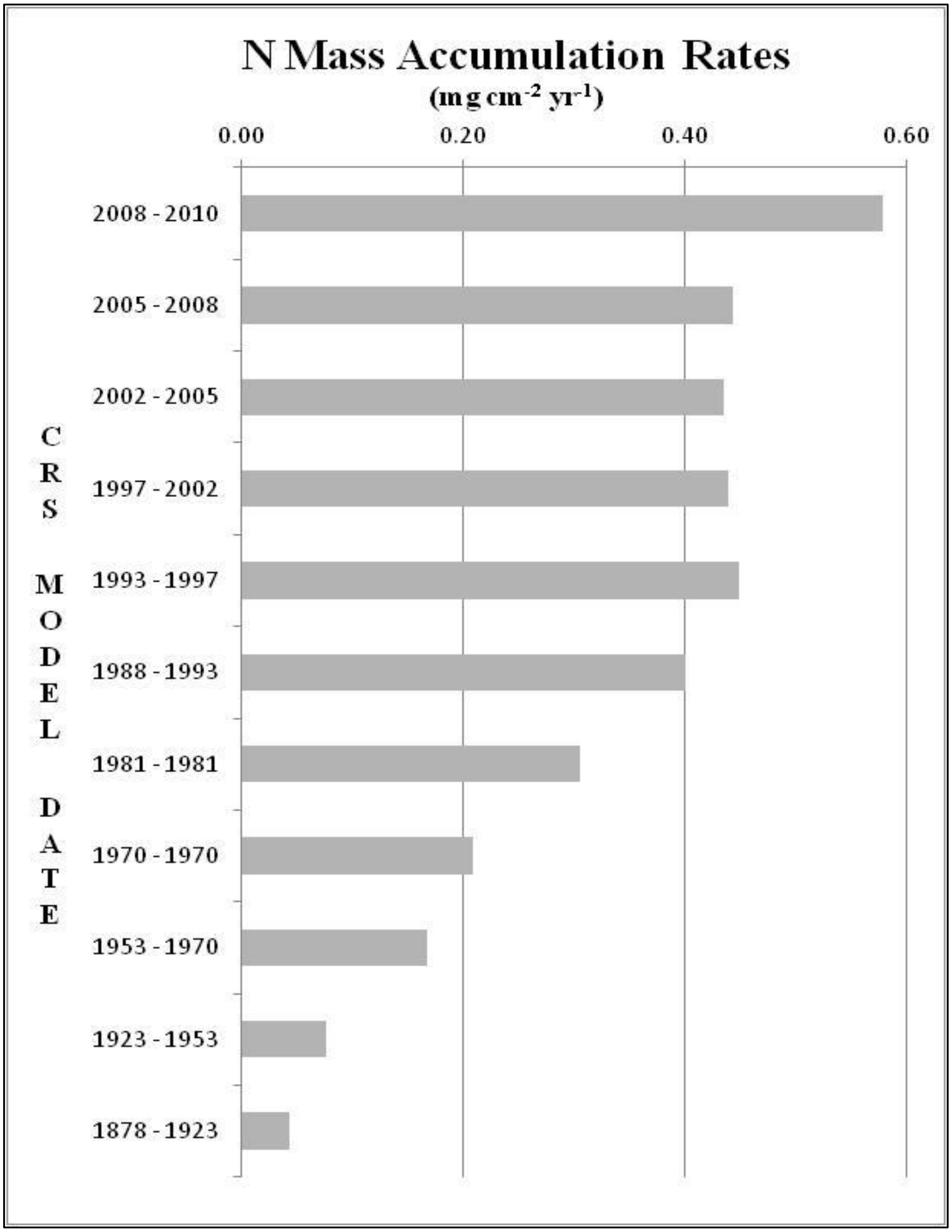

Figure 5: N Mass Accumulation Rates:

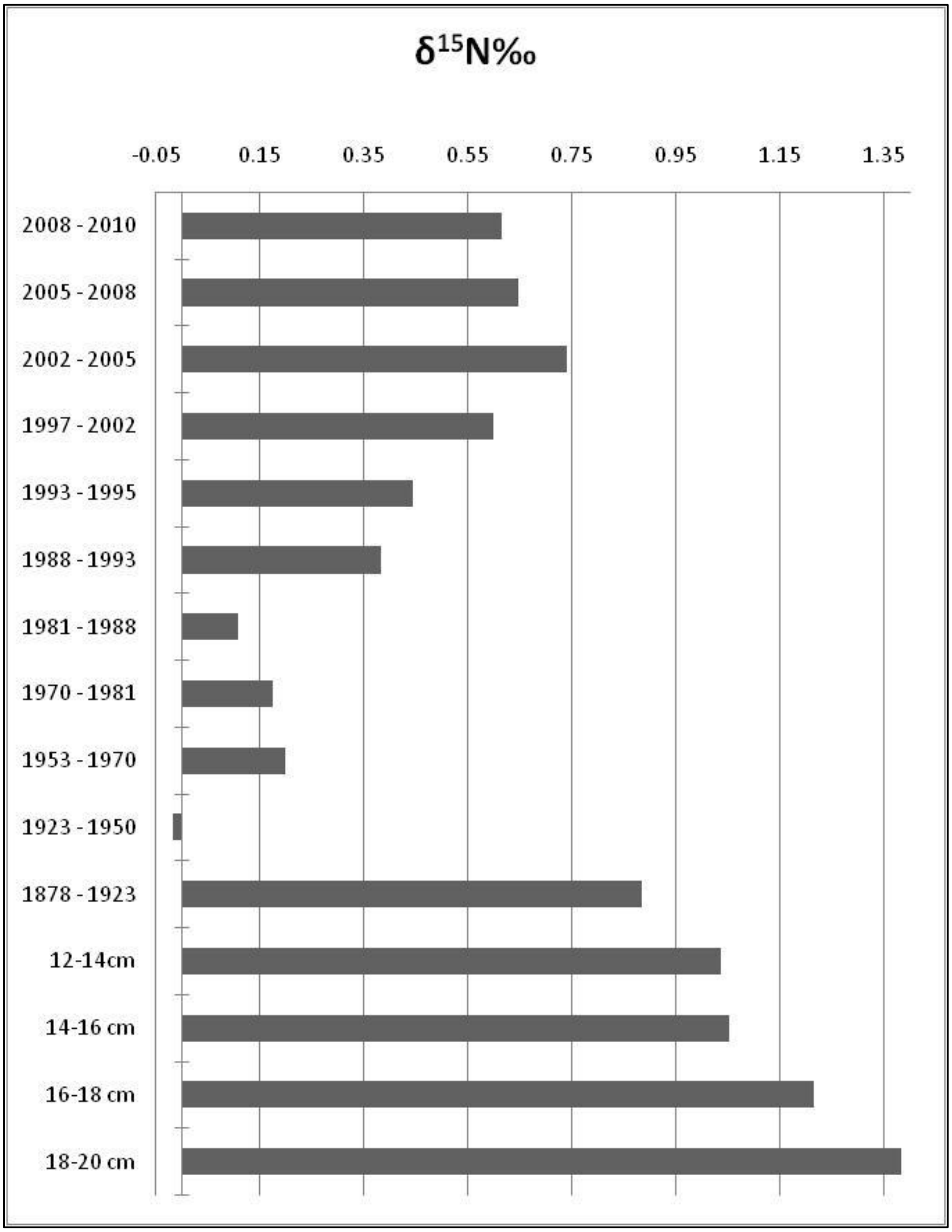

Figure 6: Dove Sound: $\delta^{15}N$‰ Bulk Sediment Values:

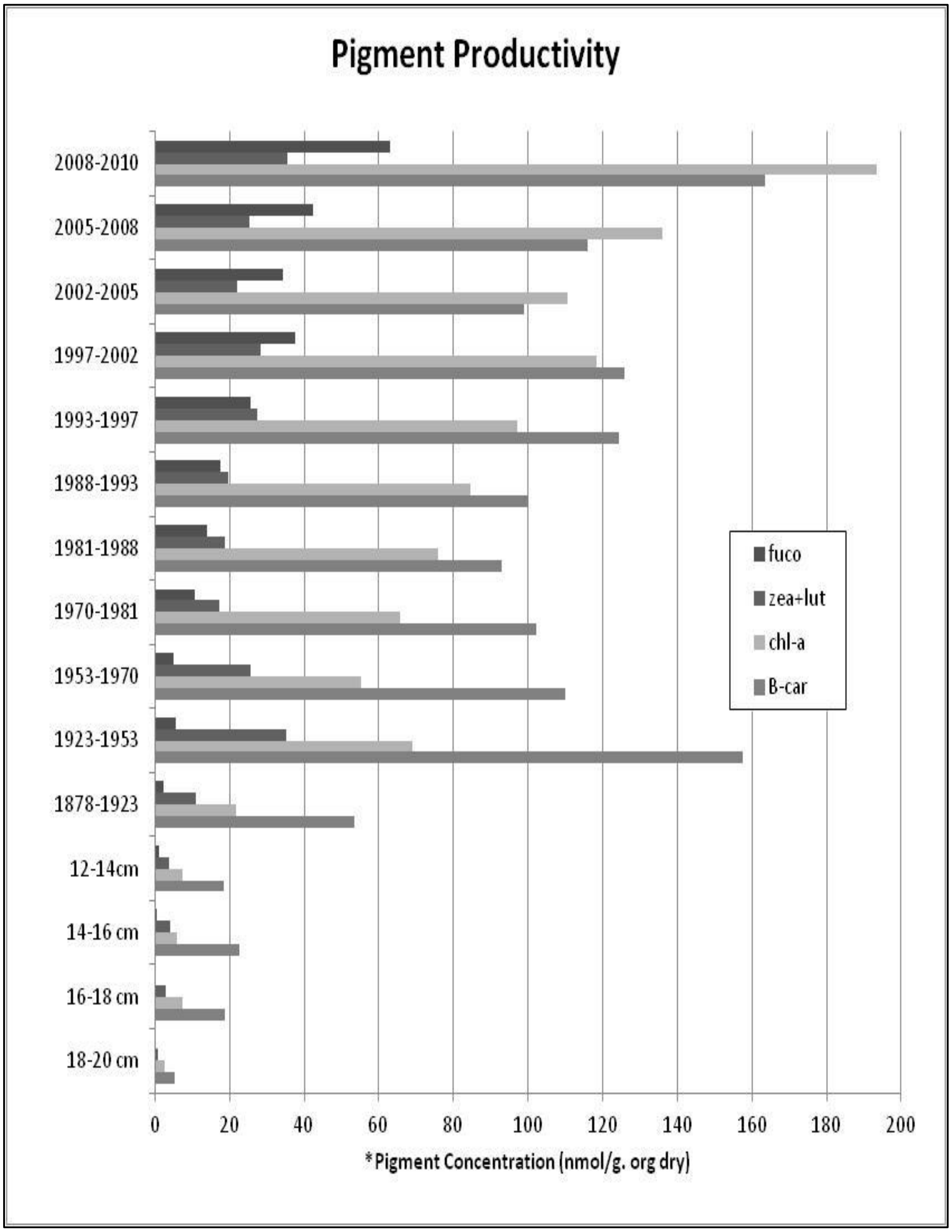

Figure 7: Major Pigments: indicator groups showing upcore productivity increases and sediment deposition as a result of increasing nutrient loading over the last 130 years. Define abbreviations used in key.

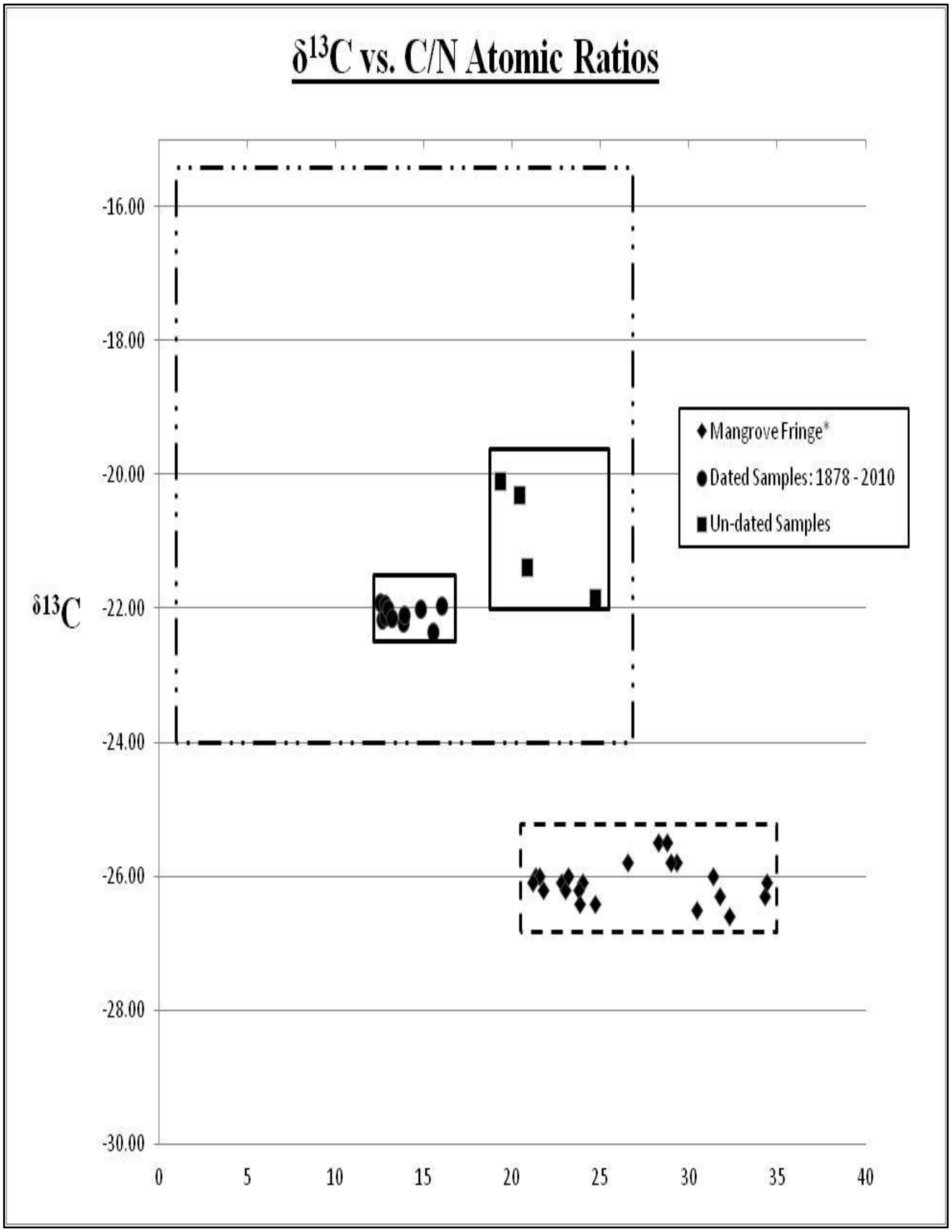

Figure 8: Isotopic Signatures For Dove Sound Core: Dated & Undated - Isotopic composition indicates marine materials and not mangrove detritus throughout core. Note the undated to dated shift of lower C/N values indicating trophic producer community transition. *Mangrove Fringe values provided by Sanders *et al.* 2010. *Multi-dash box represents culmination of previously referenced values for Florida Bay*.

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About the Author:

Thomas Snow Harmon Jr., grew up in the great hill-town of Buckland, located in Western Massachusetts, USA. He Graduated from Mohawk Trail Regional High School in 1988. He enlisted with the Massachusetts Army National Guard in 1987 in order to attend college. Mr. Harmon was awarded his A.A. from Greenfield Community College in 1996. He has lived in Indiana, Missouri, and Colorado. Currently he resides in Saint Petersburg, Florida. Mr. Harmon worked many successful careers in; mechanics, electronics, communications, and sales. Returning to school in 2007, Mr. Harmon earned his B.S. in Environmental Science from The University of South Florida in 2009. His passion for the environment motivated his continued education, further earning him a MS in Environmental Science in 2011. Mr. Harmon has presented his work at numerous conferences in regards to anthropogenic impacts on the environment. While at USF Saint Petersburg, he became the founding member of the USF Student Chapter of Environmental Professionals, from whom he was awarded a scholarship to attend the 2009 National Association of Environmental Professionals Annual Conference in Arizona.

Mr. Harmon is an avid wade fisherman and enjoys Kayaking, water sports as well as community involvement emphasizing environmental awareness at the local level. Thomas plans to continue living and working as an environmental professional while continuing to explore the greater Tampa Bay Area.