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Geochemistry of Florida Bay Sediments: Nutrient History at Five Sites in Eastern and Central Florida Bay

William H. Orem†, Charles W. Holmes‡, Carol Kendall§, Harry E. Lerch†, Ann L. Bates†, Steven R. Silva§, Anne Boylan†, Margo Corum†, Marci Marot‡, and Cheryl Hedgman†

†U.S. Geological Survey
956 National Center
Reston, VA 20192, USA

‡U.S. Geological Survey
Coastal Center
600 4th St. S.
St. Petersburg, FL 33701, USA

§U.S. Geological Survey
MS 434
345 Middlefield
Menlo Park, CA 94024, USA

ABSTRACT

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Recent seagrass dieoff and massive microalgal blooms have focused attention on the health of the Florida Bay ecosystem. Changes in nutrient input and the nutrient dynamics of Florida Bay are hypothesized to be linked to these problems, but crucial baseline information is still lacking. Efforts to restore Florida Bay to its natural condition will require information on the nutrient history of the bay. The purpose of this study was to examine distributions of organic C, total N, and total P in carbonate sediments from sites of continuous and known sedimentation rate (^{210}Pb and ^{137}Cs dated), in eastern and central Florida Bay. These sediments provide a record of historical changes in the C, N, and P load to the eastern and central bay. Analyses were conducted on sediments from cores collected at five sites, and on buried seagrass fragments at two sites. At three of the sites, sediments from seagrass-covered and adjacent barren areas were examined to determine differences in sedimentary geochemistry. Stable isotope analyses ($\delta^{13}C$ and $\delta^{15}N$) of sedimentary organic C and total N and of buried seagrass fragments were also carried out at two sites to examine possible changes in nutrient sources to the estuary.

Results were consistent with recent increases in N and P in eastern Florida Bay, beginning in the early to mid 1980's. The timing of the increase in nutrient load observed in the sediment data directly preceded the first observations of massive microalgal blooms and seagrass dieoff in Florida Bay in 1987. The observed nutrification was greater for P than N, and was most pronounced at the most northeasterly site sampled (Pass Key). Isotope data ($\delta^{15}N$) suggested that an increase in algal production accompanied the increase in N load at the Pass Key site. A long record of organic C, total N, and total P distributions from Whipray Basin in central Florida Bay showed historical peaks (mid 1700's and late 1800's) in organic C and total N, but not total P; these enrichments were nearly equivalent to recent inputs to the estuary. Barren areas were observed to have generally lower concentrations of organic C, total N, and total P in near surface sediments compared to seagrass-covered areas, but had generally similar concentrations in deeper sediments. This suggested that barren areas adjacent to seagrass-covered sites were places where relict sediment was physically transported and covered seagrass beds. This dataset provides an historical view of changes in nutrient inputs to Florida Bay, and baseline information needed for nutrient modeling of the bay.

ADDITIONAL INDEX WORDS: *Organic carbon in sediments, total nitrogen in sediments, total phosphorus in sediments, ecosystem history, The Everglades, Everglades National Park, carbon isotopes, nitrogen isotopes.*

INTRODUCTION

Florida Bay is a shallow, lagoonal estuary located between the tip of the Florida Peninsula and the Florida Keys. The bay covers approximately 2,200 km^2, with more than 80% of it located within Everglades National Park (TILMANT, 1989; ROBBLEE *et al.,* 1989). It serves as an important nursery ground for juvenile fish and invertebrates (DAVIS and DODRILL, 1989; MCIVOR *et al.* 1994), and a habitat for many wading birds, and the endangered Florida manatee and American crocodile (BANCROFT *et al.* 1994; SNOW 1991; MAZZOTTI and BRANDT, 1994). Florida Bay has an average depth of less than 1 m, and is separated into a series of shallow depressions or "lakes" by a network of mudbanks which limit circulation (SOGARD *et al.,* 1989). To the west, Florida Bay gradually merges with the Gulf of Mexico; to the east and south the Florida Keys enclose it and restrict exchange of water to narrow channels between the Keys. Freshwater flow to Florida Bay has historically been dominated by sheet flow and tidal creek discharge from Taylor Slough (Figure 1), although freshwater from the larger Shark River Slough may enter the western portion of Florida Bay by flow around Cape Sable (VAN LENT *et al.,* 1993). Another potential source of fresh-

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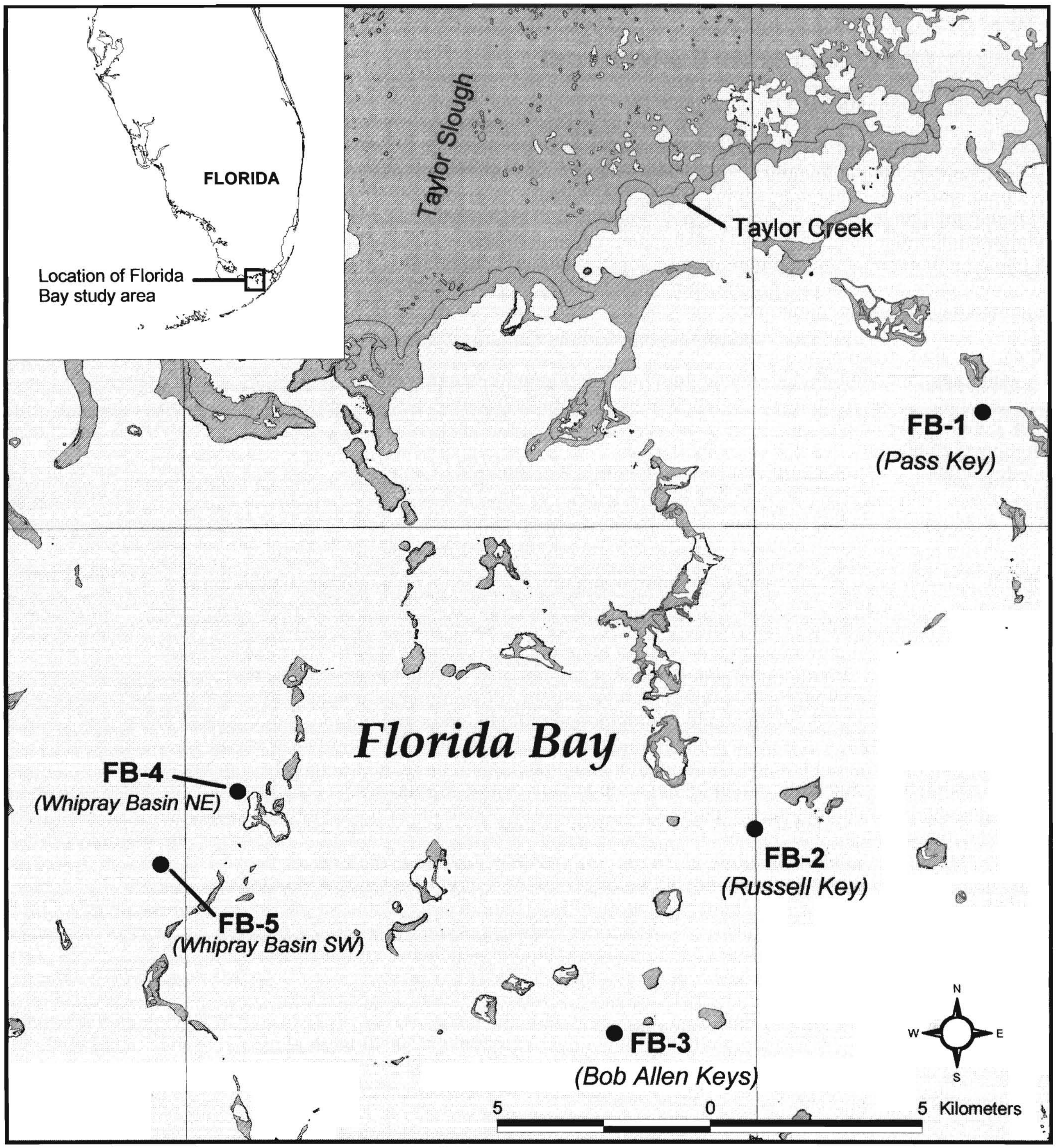

Figure 1. Location map showing the five sampling sites in eastern and central Florida Bay.

water to Florida Bay is groundwater seeping up through the porous limestone bedrock underlying the bay (SHINN *et al.*, 1996). Sediments in Florida Bay, especially in the northeastern area, are composed mostly of fine grained carbonate mud, admixed with coarse shelly material and organic debris (ENOS and PERKINS, 1978; BOSENCE, 1989).

Changes in the freshwater Everglades over the last 50 years due to extensive agriculture, urbanization, and water

Table 1. *Locations of sampling sites in eastern and central Florida Bay, and general description of sites and cores collected.*

Site	Lat.	Long.	Cores	Core Length	Sediment Thickness	Avg. Sed. Rate[1]
FB-1 Pass Key	25 08.866 N	80 34.471 W	96-33, Seagrass 96-38, Barren	80 cm 50 cm	1.2 m nd	2.06 cm/yr nd
FB-2 Russell Key	25 03.841 N	80 37.511 W	96-40, Barren 96-41, Seagrass	137 cm 114 cm	nd 1.4 m	nd 0.930 cm/yr
FB-3 Bob Allen Keys	25 01.378 N	80 39.371 W	96-51, Barren 96-56, Seagrass	80 cm 72 cm	nd 1.9 m	1.06 cm/yr 0.769 cm/yr
FB-4 Whipray Basin NE	25 04.309 N	80 44.312 W	96-46, Seagrass	81 cm	1.2 m	0.349 cm/yr
FB-5 Whipray Basin SW	25 03.432 N	80 45.325 W	97-2, Seagrass	120 cm	1.2 m	0.349 cm/yr[2]

[1] Consult HOLMES et al. (1998) for details on methods and results of sediment accumulation studies
[2] Assumed accumulation rate based on similarity of organic carbon profiles at both Whipray Basin sites

management practices have impacted Florida Bay. Diminished freshwater flow as a result of water management practices has caused periods of hypersalinity in the northeastern portions of the bay (FOURQUREAN and ZIEMAN, 1992). Seagrass (especially *Thalassia testudinum*) which once covered 80% of the bottom of the bay experienced a large dieoff beginning around 1987 (ZIEMANN *et al.,* 1989; ROBBLEE *et al.,* 1991; MCIVOR *et al.,* 1994). Massive microalgal blooms occurred in Florida Bay beginning in the mid 1980's, with a possible connection to the observed seagrass dieoff (MCIVOR *et al.,* 1994). The microalgal blooms may be tied to changes in the nutrient dynamics within the estuary, and/or the nutrient supply to Florida Bay (TOMAS, 1996), but evidence for this is sketchy. Excess nutrients (especially phosphorus) from agricultural runoff have certainly adversely affected areas of the freshwater Everglades (DAVIS, 1994), but the impact of agricultural nutrients on Florida Bay is less certain. The biogeochemistry of nutrients within the bay is complex, with the western bay possibly nitrogen limited, the eastern bay phosphorus limited, and the central bay limited by nitrogen or phosphorus depending on conditions (TOMAS, 1996). Little information is available on the biogeochemistry of nutrients in Florida Bay prior to anthropogenic changes to the south Florida ecosystem. Restoration efforts to improve conditions in the bay are, therefore, hampered by an absence of information on the natural variability of nutrients in the ecosystem.

The major objective of this study was to examine historical trends in the geochemistry of carbon (C), nitrogen (N), and phosphorus (P) within Florida Bay from dated sediment cores. Sites were carefully chosen in areas of continuous sedimentation (*e.g.* no bioturbation) so a complete record could be obtained. The sites studied vary in their sediment accumulation rates, allowing detailed historical trends to be obtained over varying time scales. A second objective was to compare the nutrient geochemistry of seagrass-covered with adjacent barren areas at selected sites to assist in developing a conceptual model of the development of barren areas. In addition to geochemical studies, sediments from cores collected at these sites were used for dating (HOLMES *et al.,* 1998), and paleoecological studies (BREWSTER-WINGARD *et al.,* 1995, 1997, and 1998). The location of the sampling sites in Florida Bay south of Taylor Slough (Figure 1) also ties in with nutrient studies being conducted in the freshwater marshes and mangrove areas of Taylor Slough (OREM *et al.,* 1998). The results of this study provide information on recent changes in nutrient inputs to Florida Bay, and an historical record of the natural variability of nutrients at five sites in the eastern and central bay.

STUDY AREA AND SAMPLING

Sediment cores were obtained from four sites in Florida Bay (Figure 1), in May and June, 1996. Three of these sites are located in eastern Florida Bay on a roughly NE to SW line (Pass Key, Russell Key, and Bob Allen Keys), and one site is located in central Florida Bay in the NE corner of Whipray Basin. Sediment samples from a fifth site (Whipray Basin SW) were collected by W. Louda (Florida Atlantic University), and graciously supplied to us for this study. GPS coordinates and general descriptions of the cores taken at each site are presented in Table 1. Cores were collected on mud banks extending out from the mangrove-covered islands at each location. At each of the sites in eastern Florida Bay, cores were taken in both seagrass-covered (*Thalassia testudinum*) and adjacent barren areas; cores were approximately 10 m from each other. The barren areas were observed to contain fragments of seagrass (*Thalassia testudinum*) buried below the surface, abundant in some cases. Cores at the Whipray Basin sites were collected only in seagrass-covered (*Thalassia testudinum*) areas.

Sediments were collected by piston coring, using a device designed and built at the U.S. Geological Survey for coring in shallow water estuarine sediments and freshwater peat environments in south Florida (OREM *et al.,* 1997a). The device consists of a monopod (pole and base), acrylic core barrel, an aluminum cutter, PVC piston with two o-rings and an eyebolt having a steel cable for attachment to the monopod, and iron handles for gripping the core barrel. Sampling sites were accessed by small boat. Water depths ranged from 30 to 100 cm. Cores were collected by (1) wading away from the boat to an undisturbed area and assembling the coring device, (2) pushing the core barrel down into the sediment with the handles (piston stationary at the sediment surface), and (3) retrieving the core by lifting up with the handles as the piston stayed fixed in place to maintain vacuum, removing the cutter and handles, and screwing a bottom cap on. A layer of surface water between the piston and sediment surface limited movement of the soupy surface sediment layer during transport. At the Russell Key and Whipray Basin SW sites coring was conducted to the bedrock. Coring stopped short of bedrock at the other sites. Care was taken to minimize impact to the seagrass beds during coring.

Cores were processed at facilities in Key Largo, FL (see Acknowledgments). Cores were sectioned into 2 cm, 5 cm, or 10 cm intervals. Each section was placed into a Ziplock plastic bag and refrigerated (4° C) for return to our laboratories in Reston, VA for further processing. Living seagrass samples collected at all sites were placed in Ziplock plastic bags and frozen for transport back to the labs. All sediment samples contained coarse material as well as fine-grained carbonate mud. Because of the presence of the coarse fraction, sediments were wet sieved prior to chemical analysis. Deionized/distilled water and brass sieves were used for wet sieving into three size fractions: >850 μm (coarse), 850–63 μm (medium), and <63 μm (fine). The coarse fraction consisted mostly of large shells and relatively complete fragments of seagrass, the medium fraction consisted mostly of broken or small shells and small broken seagrass fragments, and the fine fraction consisted exclusively of fine-grained carbonate mud. The sieved fractions were lyophilized, weighed, and stored in clean glass containers.

Trade names are used in this report for descriptive purposes only; no endorsement of products by the U.S. Geological Survey is implied.

ANALYTICAL METHODS

Organic Carbon and Total Nitrogen

The organic C and total nitrogen N contents of sediment samples were determined using a Leco 932 CHNS Analyzer (Leco Corporation, St. Joseph, MI, USA). In addition to the fine fraction of sediment, seagrass fragments from the coarse fraction at two sites (Pass Key and Bob Allen Keys) were analyzed for organic C, and total N. Only fragments visually identifiable as seagrass were analyzed. Preservation of the seagrass fragments in these highly anoxic sediments appeared to be good based on visual examination.

Total N in the sediment was measured directly, after drying the sample overnight at 60° C. Organic C was determined after removal of carbonates, which comprise the bulk of the mass of sediments from Florida Bay. We used an acid vapor method to remove the carbonates, slightly modified from that of Hedges and Stern (1984) and Yamamuro and Kayanne (1995). Sediment samples (5 to 6 mg) were weighed into prebaked (450° C) silver cups, placed in an acid vapor chamber (dessicator with beakers of concentrated HCl in the bottom), allowed to react for a minimum of 48 hrs, dried (60° C), and analyzed. In addition to samples, blanks and calcium carbonate standards were also placed in the acid vapor chamber. Blanks consisted of a prebaked (450° C) empty silver cup, and were used to monitor organic C contamination during the procedure. Calcium carbonate standards were used to visually determine when the acid vapor treatment was complete, and as a final check on the completeness of the acid vapor treatment after analysis of the standards for C on the Leco 932 CHNS analyzer.

Fragments of *Thalassia testudinum* picked from the coarse sediment fraction (0.5–1 mg for most samples) were placed in clean (baked at 450° C) glass beakers and treated with 0.5 *M* HCl to remove attached carbonates from epiphytic organisms. After treatment the samples were thoroughly rinsed with deionized/distilled water, dried (60° C) for 48 hrs and analyzed for organic C and total N.

Analytical precision is typically in the range of 1% to 4% (percentage relative standard deviation) for organic carbon, and about 1% (percentage relative standard deviation) for nitrogen.

Total Phosphorus

Total phosphorus (P) concentrations were determined by the method of Aspila *et al.* (1976), slightly modified for work in Florida Bay sediments. For the fine fraction of sediment, samples were dried overnight (60° C), cooled to room temperature in a dessicator, and then accurately weighed and placed in precleaned (soaked in 10% HCl overnight, rinsed with deionized/distilled water, and baked at 450° C) ceramic crucibles. Generally, 0.4–0.6 g of the sediment was used for the total phosphorus analysis. The weighed sediment samples were baked at 550° C for 2 hrs., cooled, then dumped into clean plastic centrifuge cones containing 45 ml of 1 *M* HCl (all plasticware used in the total P analysis was cleaned by soaking in 10% HCl overnight, followed by thorough rinsing with deionized/distilled water). The empty crucibles were rinsed with 5 ml of 1 *M* HCl and the rinse was added to the centrifuge cones for a final volume of 50 ml of 1 *M* HCl. The samples were extracted in the 1 *M* HCl for 16 hrs. on a shaker bath to dissolve the phosphate. An aliquot of each extract was centrifuge filtered using clean Millipore ultrafree-CL HVPP low-binding Durapore centrifuge filters (0.45 μm pore size), then neutralized with a NaOH solution, and transferred to clean plastic test tubes. The filtered aliquots were then analyzed for phosphate using the standard phospho-molybdate method (Strickland and Parsons, 1972), and a Brinkman PC900 fiberoptic colorimeter. Results are reported as μg P/g sediment on a dry weight basis. Analytical precision for the total P analysis is about 3% (percentage relative standard deviation).

Stable Isotope Analysis

At Pass Key and Bob Allen Keys, the organic C and total N in the fine fraction and in seagrass fragments picked from the coarse sediment fraction were analyzed for stable isotopic composition ($\delta^{13}C$ and $\delta^{15}N$) using a Micromass Optima continuous flow mass spectrometer coupled to a Carlo Erba elemental analyzer. Samples were analyzed for $\delta^{13}C$ and $\delta^{15}N$ before and after acidification to remove carbonates; the $\delta^{15}N$ value prior to acidification and the $\delta^{13}C$ value after acidification (representing the organic fraction of the sediment). Carbonates were removed from the samples using the acid vapor method (Hedges and Stern, 1984; Yamamuro and Kayanne, 1995), except that the samples were acidified for

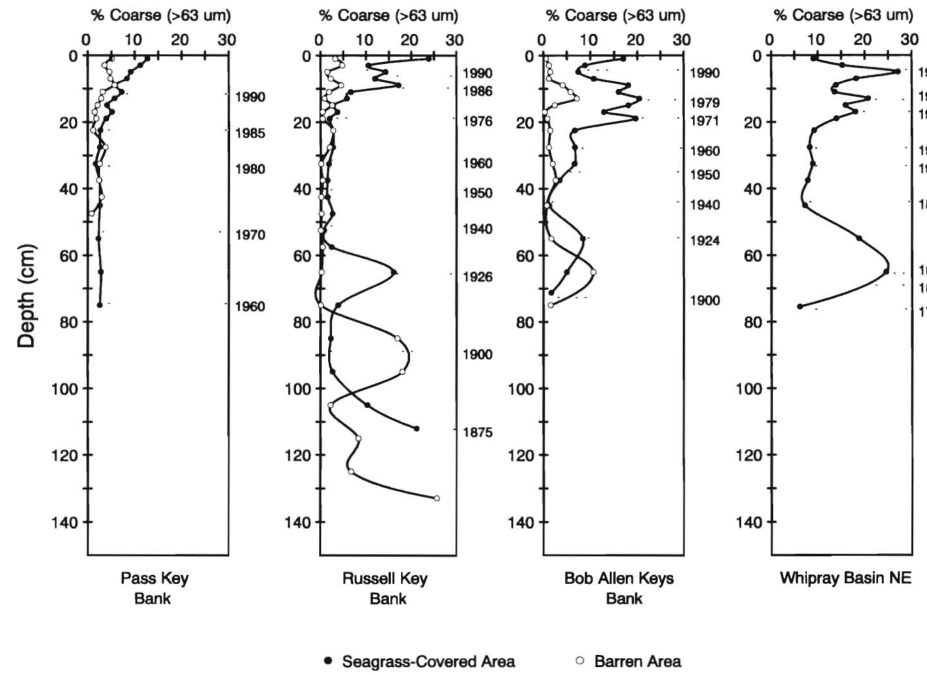

Figure 2. The percentage of coarse sediment (>63 μm) versus depth at four sites in Florida Bay. At three sites, distributions in barren and seagrass-covered areas are differentiated.

18 hrs after being moistened with deionized/distilled water. Results are reported in the usual delta format as permil values (CRAIG, 1957; MARIOTTI, 1983): (1) for ^{13}C relative to V-PDB, normalized to a scale where NBS-19 is +1.95 permil and NBS-21 is −28.10 permil, and (2) for ^{15}N relative to air, normalized to a scale where IAEA-N1 is +0.43 permil and IAEA-N2 is +20.41 permil. Analytical precision (1 sigma level) was generally in the range of 0.1 to 0.2 permil for both C and N, but for some seagrass samples replication was no better than ± 0.5 permil due to sample heterogeneity and the difficulty of grinding the small seagrass fragments.

Age Dating of Sediment Cores

Duplicate cores from each of the sampling sites, with the exception of Whipray Basin SW, were dated using ^{210}Pb and ^{137}Cs analysis (HOLMES *et al.,* 1998). Calculation of sedimentation rates at each site from ^{210}Pb data (Table 1) used the constant rate of supply (CRS) model (BINFORD, 1990; HOLMES *et al.,* 1998). Sediment dating was not conducted at the Whipray Basin SW site, however, the similarity of downcore organic C and total N profiles at the Whipray Basin NE and SW sites (Figures 3 and 4) suggested that the sedimentation rate was similar at these two sites.

RESULTS AND DISCUSSION

Sediment Size Analysis

In the sediment size distribution plots for the seagrass-covered and barren areas (Figure 2), the coarse (>850 μm) and medium (850–63 μm) fractions were combined and designated simply as coarse (>63 μm) for illustrative purposes. In general, the downcore profiles of the >850 μm and 850–63 μm fractions closely paralleled each other, and little information was lost in combining these fractions. Sediment size data were not collected for the Whipray Basin SW site due to sample size limitations.

Overall, the >63 μm size fraction varied from about 27% to less than 1% of the total sediment mass. Whipray Basin appeared to have the coarsest sediment overall, and Pass Key the finest. A general trend of increasing sediment size toward the surface was observed at Pass Key, Russell Key, and Bob Allen Keys. This trend could have been due to winnowing at or near the sediment surface or greater seagrass abundance (with concomitant greater shell input to the sediments from epiphytic organisms on the seagrass) in recent times. At Whipray Basin NE increased coarsening towards the surface from 20 cm to about 5 cm was observed, followed by a sharp decrease in sediment size from 5 cm to the surface. The finer sediment at the surface could have resulted from movement of fine-grained sediments to this site, and represent the beginning of the burial of this seagrass bed.

Barren areas at Pass Key, Russell Key, and Bob Allen Keys had distinctly finer sediments near the surface compared to seagrass-covered areas (Figure 2). Further downcore, however, the sediment size profiles of the barren and seagrass-covered areas were similar. Seagrass fragments were found at depth in the cores from barren areas, and suggested that fine sediment had moved into former seagrass beds, ultimately burying them. The origin of this fine-grained sediment and the physical controls on its movement into seagrass beds is unclear.

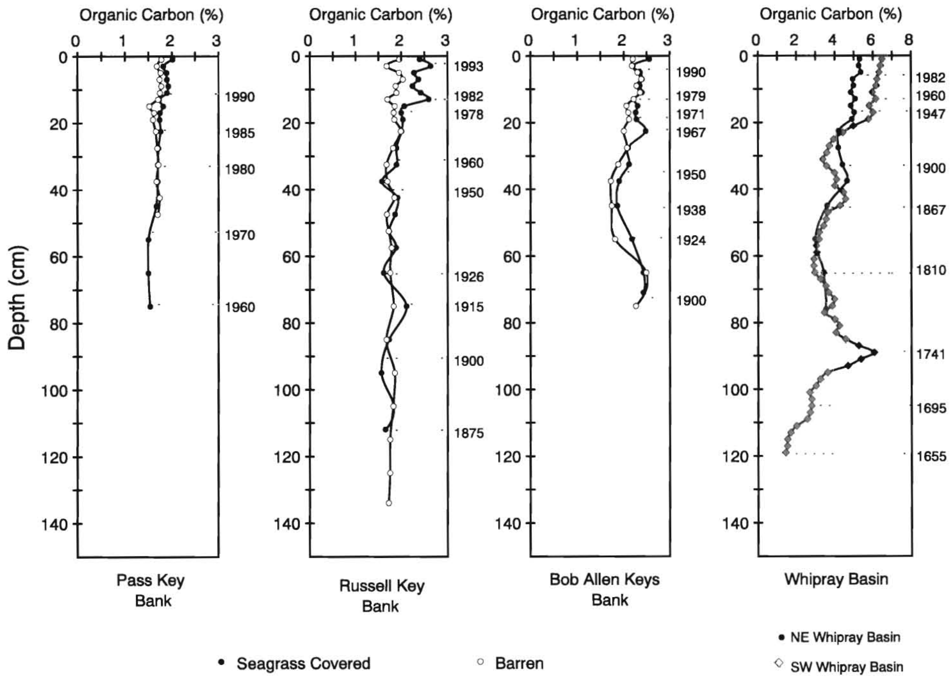

Figure 3. Organic carbon distribution (% dry wt.) in the fine (<63 μm) sediment fraction at five sites in Florida Bay.

Historical changes in the downcore sediment size profiles at these sites may have reflected changes in seagrass abundance, as mentioned. Changing physical processes within the estuary such as circulation patterns, however, could also have been responsible for the observed variation in sediment size distribution. The Pass Key core, with a short historical record, showed only a gradual decline in sediment size with depth. At Russell Key the following intervals were observed at the seagrass site: (1) a coarse interval (up to 23% coarse) at the base of the core, about 1875 to about 1895, (2) a period of mostly fine sediment accumulation (<5% coarse) between about 1895 and 1915, (3) an interval of coarser sediment around 1926 (17% coarse), (4) a long interval of fine sediment accumulation (<5% coarse) from about 1930 to 1976, and (5) a period of sediment coarsening after 1976 to the present, but with a decline in the coarse fraction in the period around 1989 to 1993.

The historical record of sediment size at the Bob Allen Keys seagrass site showed some similarities to that of Russell Key: both cores exhibited a large increase in coarse sediment from about 1925–1926, and a decrease in coarse sediment from 1990–1993. Differences were apparent too. For example, the Bob Allen core did not exhibit the period of very fine sediment accumulation between 1930 and 1976 observed at Russell Key. Sediments with <5% coarse material at Bob Allen were only observed in the period from about 1935 to 1950. Also, the near-surface increase in coarse sediment occurred earlier at Bob Allen (after 1965, with some coarsening as early as 1950), compared to Russell Key (beginning after 1976).

The core from the Whipray Basin NE site contained a much longer record of sediment accumulation. This site had coarser sediments overall compared to the other sites. Nevertheless, significant changes in the historical record of sediment size were seen: (1) fine sediment (about 5% coarse) at the bottom of the core (about 1781), transitioning to coarser sediment with a peak about 1810 (25% coarse), (2) a relatively finer sediment (5–10% coarse) deposited between 1867 and 1930, (3) a general increase in coarse sediment after about 1940, with various peaks (1947, 1960, and 1982) and valleys (1953, and 1964–70), and (4) a sharp decrease in sediment size in the upper 4 cm of sediment (1982 to present). The downcore sediment size distribution at Whipray Basin NE did not correlate with the profiles at the other sites.

Geochemistry of Fine Sediment Fraction

Organic C and Total N

Concentrations of organic C (% dry wt.) ranged from about 1.5% to nearly 7% in the cores (Figure 3). The overall highest concentrations of organic C were observed in the Whipray Basin cores, and the lowest concentrations at Pass Key. This difference reflected the much higher sedimentation rate at Pass Key compared to Whipray Basin (Table 1), with fine grained carbonate sediment (low organic carbon content) diluting the accumulating organic carbon at Pass Key. In contrast to the concentration data, the highest accumulation rates (Table 2) for organic C were at Pass Key (200–330 gC/m^2-yr), and the overall lowest accumulation rates at the Whipray Basin NE site (43–110 gC/m^2-yr). Accumulation rates were calculated using sedimentation rates (HOLMES *et al.,* 1998), dry bulk density of the sediment (HOLMES and MAROT, unpublished data), and organic C concentrations for

Table 2. *Organic C, total N, and total P accumulation rates (AR) at four sites in Florida Bay.*

Sample	Depth (cm)	AR Org. C (gC/ $m^2 \cdot yr$)	AR Total N gN/ $m^2 \cdot yr$	AR Total P gP/ $m^2 \cdot yr$
FB-1	1	210	27	1.2
Pass Key Seagrass	9	260	36	1.6
	15	250	33	1.6
	22.5	240	30	1.2
	32.5	240	31	1.2
	45	300	36	1.5
	55	300	36	1.5
	65	300	34	1.6
	75	330	38	1.7
FB-2	1	69	8.3	0.42
Russell Key Seagrass	3	64	7.5	0.34
	9	71	9.2	0.38
	13	135	15	0.61
	15	71	7.9	0.34
	22.5	110	13	0.50
	32.5	130	14	0.63
	42.5	130	14	0.51
	52.5	130	14	0.46
	65	140	15	0.58
	75	180	18	0.62
	85	150	14	0.66
	95	140	14	0.58
	105	190	18	0.67
	112	160	17	0.61
FB-3SG	1	28	3.4	0.13
Bob Allen Keys Seagrass	9	78	10	0.32
	15	130	17	0.52
	22.5	160	20	0.70
	32.5	120	15	0.52
	45	100	12	0.46
	55	130	15	0.55
	65	140	18	0.66
	71	160	20	0.72
FB-3B	1	130	15	0.58
Bob Allen Keys Barren	9	170	19	0.62
	15	180	20	0.70
	22.5	200	21	0.83
	32.5	170	18	0.77
	45	190	20	0.89
	55	190	20	0.95
	65	210	22	0.91
	75	230	24	1.0
FB-4	1	43	5.4	0.18
Whipray Basin NE Seagrass	9	96	12	0.35
	15	110	13	0.39
	22.5	90	11	0.30
	32.5	97	13	0.29
	37.5	86	12	0.31
	45	74	10	0.36
	55	61	8.2	0.35
	65	75	9.0	0.28
	75	88	13	0.37

the various depth intervals at these sites. Accumulation rates for the Whipray Basin SE site were not calculated because dry bulk density data were unavailable.

At Pass Key and Russell Key, barren areas had generally lower organic C contents than seagrass-covered areas in the upper sections of the cores. At Russell Key, the difference in organic C content between barren and seagrass-covered areas exceeded 1% in some intervals. At depth, barren and seagrass-covered areas had generally similar organic C profiles. Where differences occurred, there were no consistent patterns. At Bob Allen, there was little difference between the organic C contents of sediments from barren and seagrass-covered areas near the surface. Below 15 cm., however, the barren area had consistently lower organic C contents. Accumulation rates of organic C (Table 2) were considerably higher at the Bob Allen Keys barren area, compared to the adjacent seagrass-covered area. This was due to the higher sedimentation rate and higher bulk density at the barren site. Accumulation rates at the other barren sites (Pass Key and Russell Key) were not presented as sedimentation rates were unavailable.

Changes in the downcore profiles of organic C (Figure 3) reflected both diagenetic alteration of organic C (BERNER 1971; MACKO *et al.* 1993), and historical changes in the supply of organic C to the sediments. At Pass Key, the downcore profile showed only a gradual decline in organic C with depth, probably reflecting diagenetic alteration of organic matter. At the Russell Key seagrass site, peaks in organic C content are present in the surface zone (1982 and 1993), and near 75 cm (about 1915). At the Bob Allen Keys seagrass site, a peak in organic C at the base of the core was observed, with a date of around 1900–1915. This peak corresponded to the peak in organic C at Russell Key around 1915. Another peak in organic C at Bob Allen was present with a date of about 1967. The overall trend at Bob Allen showed a peak in organic C in the early 1900's, very low levels between 1930 and 1950, and generally higher values since the 1950's.

The long sediment records from Whipray Basin showed several large anomalies in organic C content in the downcore profiles (Figure 3). The organic C profiles at the two sites were similar, suggesting that the environmental processes controlling organic C deposition acted across Whipray Basin. The similarities in the profiles also suggested that the sedimentation rate and dates available for the NE site in Whipray Basin were also applicable to the SW site. At the Whipray Basin SW site, the downcore profile for organic C had the following trends: (1) very low organic C content (about 1%) at the base of the core (1655), with gradually rising values after this, (2) a peak in organic C content at an estimated date of 1741, with a peak concentration (6.1%) that approached surface sediment concentrations (6.5%), (3) gradually falling organic C, with concentrations minimizing at 2–4% from around 1800 to 1865, (4) another peak in organic C (concentration >5%) from about 1865 to 1875, (5) another region of relatively low organic C (2–3%) from around 1880 to 1920, and (6) gradually increasing organic C (>6%) from about 1920 to the present. Differences in the organic C profiles between the cores at the two Whipray Basin sites were: about 1% lower organic C contents in the near surface sediments at the Whipray Basin NE site, and a slight offset in the late 1800's peak in organic C between the two sites.

Total N contents of sediments (% dry wt.) at the five sites ranged from about 0.15% to 0.82% (Figure 4). General trends in total N were similar to those for organic C, including: (1)

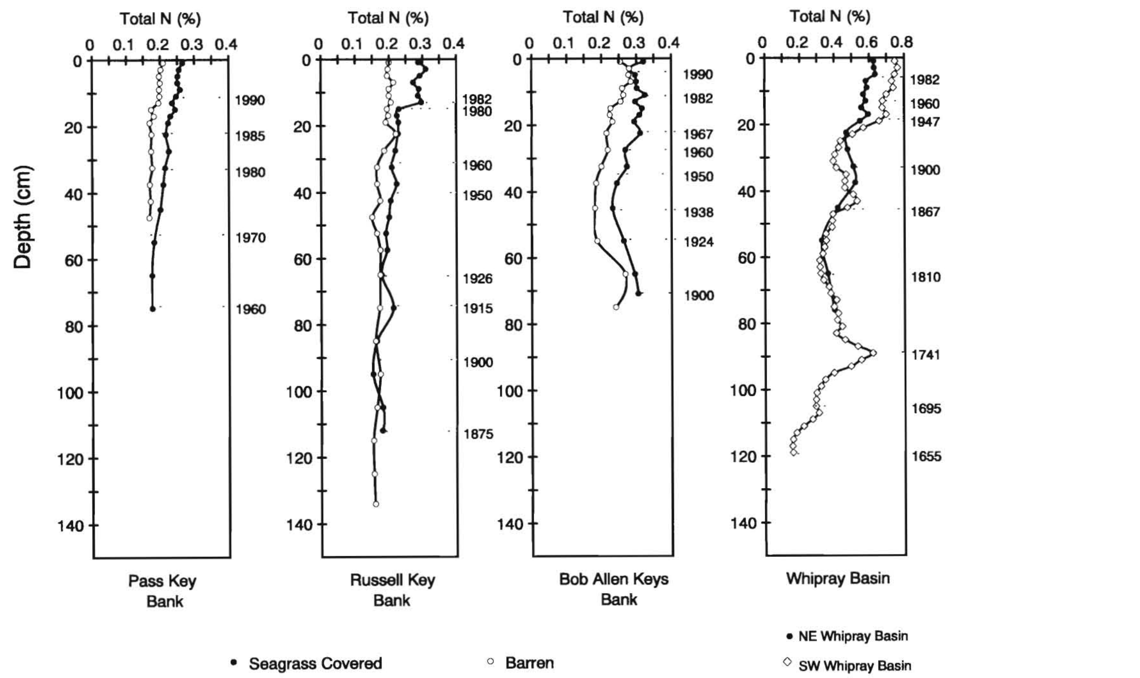

Figure 4. Total nitrogen distribution (% dry wt.) in the fine sediment fraction for the same locations as in Fig. 3.

highest concentrations for total N in Whipray Basin and the lowest concentrations at Pass Key, (2) total N accumulation rates highest at Pass Key and lowest at Whipray Basin NE (Table 2), and (3) barren areas with generally lower total N contents than seagrass-covered areas. The differences between barren and seagrass-covered areas, however, were somewhat greater for total N than for organic C. Downcore profiles of concentration and accumulation rate for total N at all sites closely paralleled those for organic C (Figure 4 and Table 2).

Total Phosphorus

Concentrations of total P at the five sites in Florida Bay ranged from 50 to 250 μg/g (dry wt.), (Figure 5). In surface sediments, total P concentrations ranged from 100 to 250 μg/g. This compared to values of 300 to 500 μg/g P in surface peats of the freshwater Everglades to the north (Shark River Slough and Taylor Slough), and concentrations of 400 to 700 μg/g P in surface sediments from the mangrove fringe area of Florida Bay (OREM *et al.,* 1997b). Total P concentrations were lowest at Pass Key and highest in Whipray Basin. Accumulation rates for P (Table 2) were highest at Pass Key (1 to 2 gP/m^2-yr), and lowest at Whipray Basin (0.1 to 0.4 gP/m^2-yr), reflecting the higher sedimentation rate at Pass Key.

At Pass Key and Russell Key, total P concentrations in surface sediments from barren areas were generally lower than those in nearby seagrass-covered areas. This was also true for organic C and total N, as mentioned earlier. The difference in total P concentrations between barren and seagrass-covered areas was as much as 50 μg/g at Russell Key. At depth, the total P concentrations of barren and seagrass-covered areas from Pass and Russell Keys were generally similar. At Bob Allen, total P concentrations of sediments from the barren area were only slightly lower than those in the seagrass-covered area.

Downcore variations in total P concentrations reflected both diagenesis and changes in P supply to the sediments. At the Pass Key seagrass site, little variation in the concentration of total P in sediments was apparent prior to about 1985, with values in the range of 77 to 88 μg/g (Figure 5). After 1985, concentrations of total P in these sediments exhibited a sudden increase to concentrations in excess of 120 μg/g (peak values in 1989 and 1992). At the Russell Key seagrass site, the overall downcore trend was one of decreasing total P concentration with depth. Prior to 1950, concentrations at the Russell Key seagrass site showed little variation, ranging from 60 to 75 μg/g. After 1950, concentrations of total P at Russell Key increased, with the greatest rate of increase observed after 1982. At the Bob Allen Keys seagrass site, little variation in total P concentration was observed downcore. Slightly higher P concentrations were seen at Bob Allen during the early 1900's (1900–1912), the late 1960's (peak in 1967), and at the surface. The period of lowest total P concentrations at this site occurred from about 1925 to 1950.

In the two Whipray Basin cores, downcore variations in total P concentrations were similar. Similarities in the downcore profiles of organic C and total N were also observed at the two Whipray Basin sites. Overall, the P profiles showed the following trend: (1) little variation in total P concentration before 1730 (concentrations averaging around 136 μg/g), (2) an increase in total P beginning after 1730, with peak concentrations approaching 193 μg/g during the mid 1800's

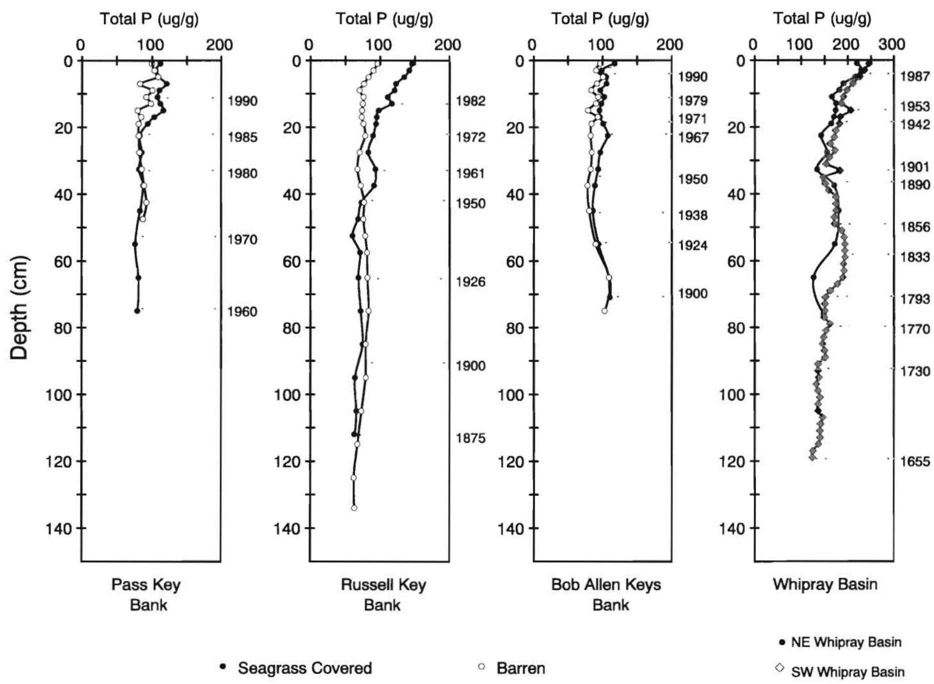

Figure 5. Total phosphorus distribution (% dry wt.) in the fine sediment fraction for the same locations as in Fig. 3.

(the precise timing of this peak in total P varies between the two Whipray cores), (3) decreasing total P concentrations by the late 1800's, with relatively low total P values persisting until about 1940, (4) increasing total P concentrations after about 1940 to the surface, with the greatest rate of increase after 1960. The peak in total P during the 1800's at the Whipray Basin site may correspond to the peak in total P observed at the base of the core at Bob Allen. Note that the total P profile exhibited no large peak at 79 cm (1741), as was observed for organic C and total N. The two Whipray Basin sites and all sampling sites except Bob Allen had the highest concentrations of total P in the near surface zone, 1950 and later.

Total P accumulation rates generally increased with increasing sediment depth (Table 2). This trend was largely driven by changes in the dry bulk density of the sediments, which increased with increasing sediment depth (Holmes and Marot, unpublished data).

Atomic C/N, C/P, and N/P Ratios

Downcore profiles of atomic C/N, C/P, and N/P ratios in sediments from all five sites are presented in Figures 6, 7, and 8, respectively. Atomic C/N values (Figure 6) were generally in the range of 9 to 12, but values as low as 8.3 and as high as 13.1 were observed. Atomic C/N values of Florida Bay sediments were much lower than those observed in the southern Everglades (Shark River Slough and Taylor Slough), where atomic C/N values generally exceeded 20 (Orem, unpublished data). This reflected the greater N content of organic matter derived from algae compared to vascular plants (Tissot and Welte, 1984), with a greater algal contribution to the organic matter in Florida Bay sediments and a greater vascular plant contribution to peat from the Everglades. Seagrass (vascular plants) also contributed to the organic matter in sediments from Florida Bay. Atomic C/N values for fresh seagrass (*Thalassia testudinum*) were 15 to 16, while buried seagrass fragments had C/N values generally ranging from 20 to 40. Barren sites had generally higher atomic C/N values than seagrass-covered sites, reflecting the generally lower N contents of the sediments from barren areas.

The most distinctive feature of the atomic C/N plots (Figure 6) was the trend toward lower C/N values near the surface at the Pass Key and Russell Key seagrass sites. This was most apparent at Pass Key, where a shift in atomic C/N towards lower values occurred above 22.5 cm (after 1985). At Russell Key, the change to lower atomic C/N values occurred above 15 cm (after 1980), but was less pronounced than at Pass Key. At the seagrass-covered Bob Allen site there was a shift toward lower atomic C/N values from about 1971 to 1987, but a shift back to higher values after 1987. The barren areas at Pass Key and Bob Allen Keys also showed a shift to lower atomic C/N values near the surface with about the same timing as that at the seagrass-covered areas. The Russell Key barren area exhibited an irregular pattern in atomic C/N values near the surface.

Below the surface zone, the principal change (if any) observed downcore in the atomic C/N values was a slow increase with depth. This observed trend was likely due to preferential utilization of N-containing organic matter by anaerobic bacteria in the sediments (Macko *et al.*, 1993). Both cores from Whipray Basin were nearly coincident, and exhibited only a gradual rise in atomic C/N with depth. Similarly,

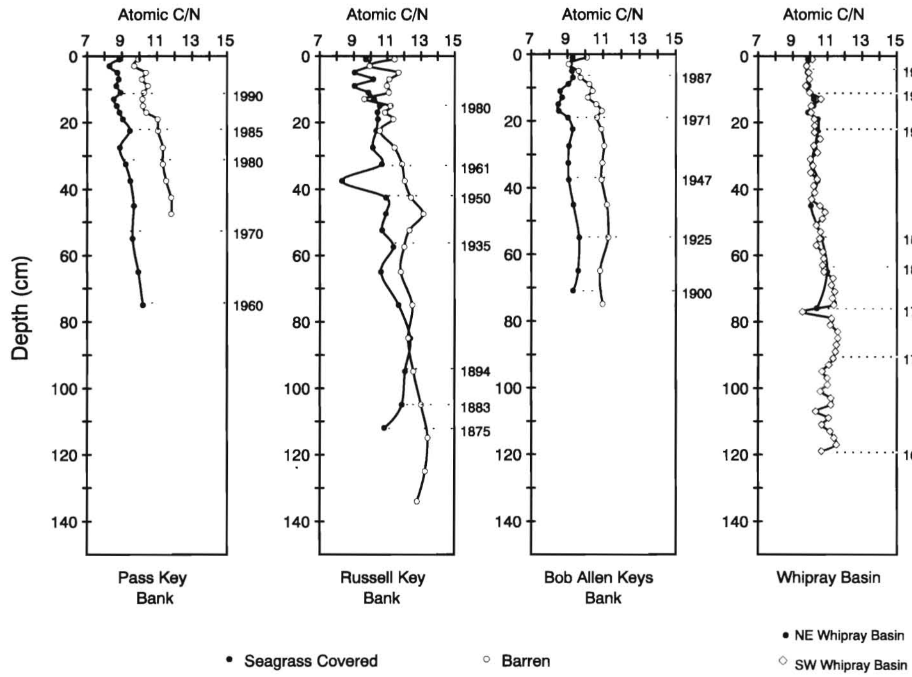

Figure 6. Atomic carbon/nitrogen (C/N) ratio in the fine sediment fraction for the same locations as in Fig. 3.

barren and seagrass-covered areas at Pass Key showed only a gradual increase in atomic C/N with depth below the surface zone. The barren and seagrass-covered areas at Bob Allen exhibited minimal change in atomic C/N below 20 cm. The barren and seagrass-covered areas at Russell Key showed somewhat more irregular downcore profiles of atomic C/N below 20 cm, but the overall change was still a gradual increase in values with depth.

Atomic C/P ratios ranged from 1,040 to 300, but with most values between 400 and 900 (Figure 7). Much higher atomic C/P values (2,000 to 7,000 in pristine areas) were observed in peat from the lower freshwater Everglades (OREM, unpublished data), and reflected the much lower total P content of vascular plants (the major contributor to organic matter in peat) compared to algae (TISSOT and WELTE, 1984). The lower atomic C/P values in Florida Bay sediments is indicative of the greater algal input to organic matter in the bay sediments compared to peat from the Everglades. In the surface sediments there was a geographic distribution of increasing atomic C/P values from north to south and east to west in these cores. This could indicate a P source to the north and east. The upper sediment layers from barren areas had generally higher atomic C/P values than seagrass-covered areas (above 22 cm at Pass Key, above 42 cm at Russell Key, and above 32 cm at Bob Allen Keys). At depth, the profiles of atomic C/P at barren and seagrass-covered areas were similar at the Pass Key and Bob Allen Keys sites. At Russell Key, the barren site had systematically lower C/P values compared to the seagrass-covered area below 42 cm.

The most distinctive feature of the atomic C/P profiles in Figure 7 was the abrupt drop in values observed in the near surface zone. This was most apparent at the Pass Key seagrass site, where values declined from 547 at 22.5 cm (1985) to between 398 and 465 near the surface. The C/P ratio was also very low (427) at 37.5 cm (1978). At the Russell Key seagrass site, the drop in C/P values occurred earlier: (1) values fell from about 700 at 42.5 cm (1950) to about 450 at 37.5 cm (1956), (2) then increased to values of 520 to 590 from about 1961 to 1982, and (3) finally declined above 11 cm (1982) to an atomic C/P value of 424 at the surface. A low in atomic C/P values was also observed between 85 and 95 cm (1894–1905) at Russell Key, primarily due to low organic C content. At both sites in Whipray Basin, atomic C/P values declined in the near surface: at the NE site from 755 (1959) to 624 at the surface, and at the SW site from 811 at 13 cm to 681 at the surface. The surface atomic C/P values at the Whipray Basin sites, however, were not historic lows. Other periods of very low atomic C/P values were observed between 1903 and 1932, about 1810 to 1873, and at the base of the core (about 1655–1700). The atomic C/P profiles closely paralleled the organic C profiles at the Whipray Basin sites. Thus, the variation observed in the downcore atomic C/P values was driven largely by changes in the organic C content of the sediment rather than changes in total P. The minimum in the C/P profile between 1810 and 1873, however, coincided with a rise in the total P content at both Whipray sites (Figure 5). At Bob Allen, little change in atomic C/P was observed in the downcore profile, with only a slight decline in values above 9 cm (1984).

Atomic N/P values ranged from about 25 to 88 at the Florida Bay sites (Figure 8). These values were somewhat lower than atomic N/P values for peats from the lower Everglades

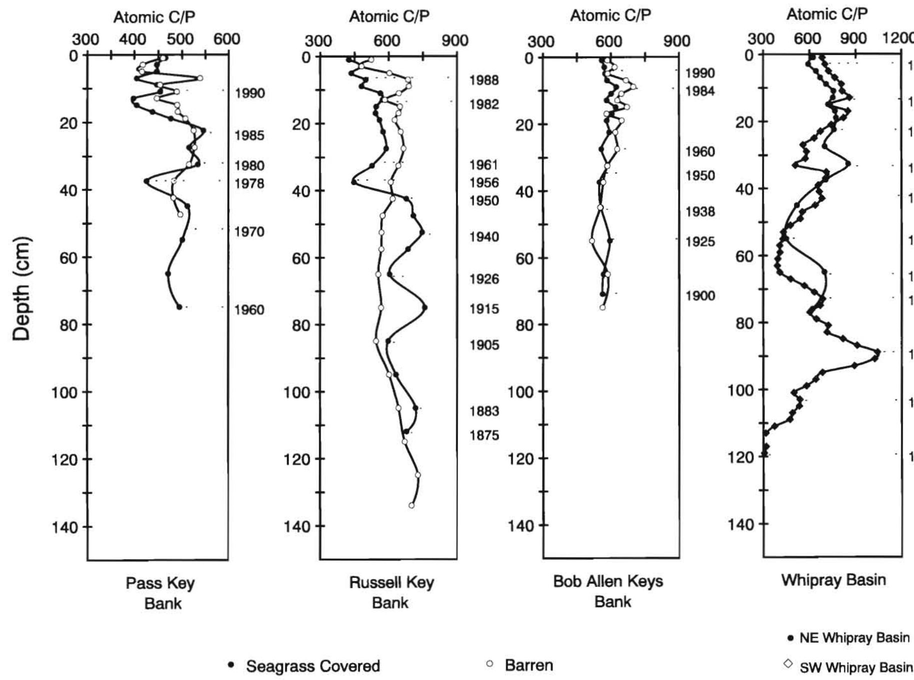

Figure 7. Atomic carbon/phosphorus (C/P) ratio in the fine sediment fraction for the same locations as in Fig. 3.

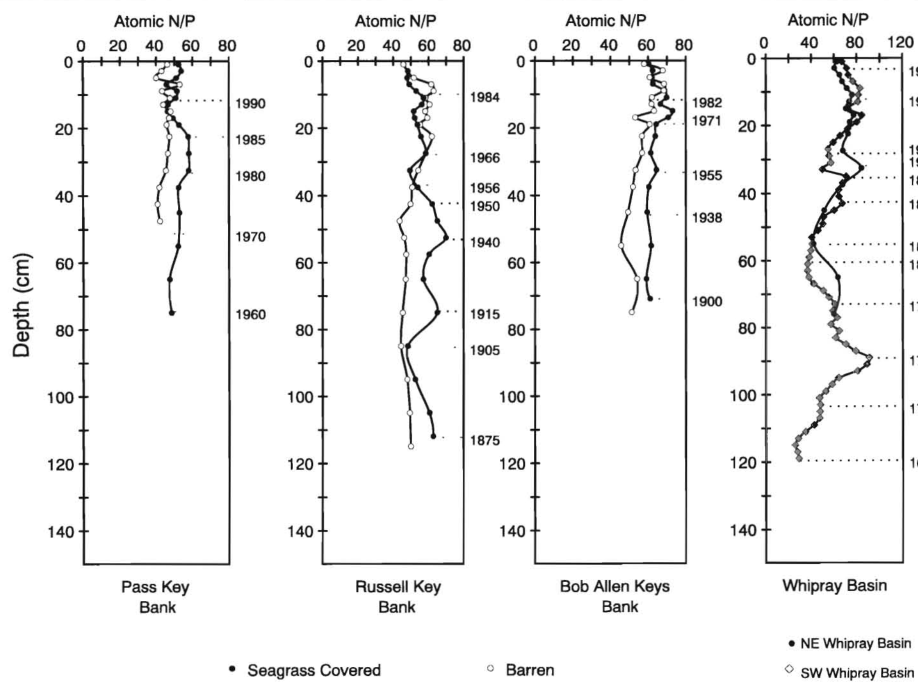

Figure 8. Atomic nitrogen/phosphorus (N/P) ratio of the fine sediment fraction for the same locations as in Fig. 3.

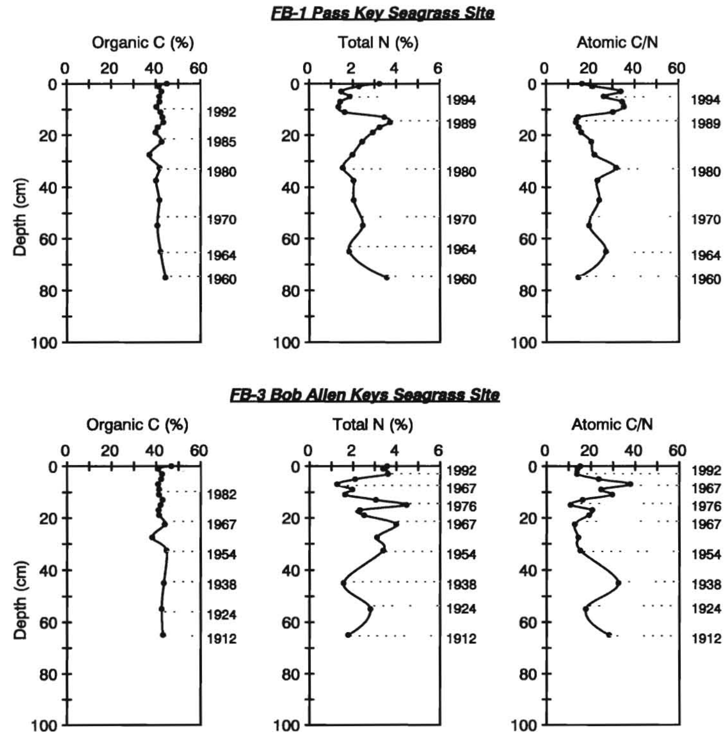

Figure 9. Organic carbon (% dry wt.), total nitrogen (% dry wt.), and atomic carbon/nitrogen (C/N) ratios of living seagrass, *Thalassia testudinum,* and buried *Thalassia testudinum* fragments in sediments from the Pass Key and Bob Allen Keys sites in Florida Bay. Values for the living seagrass are shown at depth = 0 cm.

and mangrove fringe area, which generally ranged from 80 to 300 (OREM, unpublished data). Thus, the freshwater peat environment may be more P limited than Florida Bay. Whole core atomic N/P values increased to the south and west in the following order: Pass Key < Russell Key < Bob Allen Keys < Whipray Basin SW ≈ Whipray Basin NE. Barren and seagrass areas had generally similar atomic N/P values in the upper sediment zone (*e.g.* above 17 cm at Pass Key, 37.5 cm at Russell Key, and 11 cm at Bob Allen Keys). At depth, however, sediments from barren areas had generally lower atomic N/P values, which reflected the lower N content of sediments from the barren areas (Figure 4). Recent increased algal productivity in the surface water could account for the similarity in the N/P values of barren and seagrass-covered areas in the upper sections of the cores, as this would likely impact both areas similarly.

Downcore changes in atomic N/P values were observed at all sites (Figure 8). At Pass Key, the most significant feature of the profile was the sharp decrease in values between 1985 and 1990. This change coincided with the decreases in atomic C/N and C/P discussed earlier (Figures 6 and 7), and showed that P concentrations were increasing faster than N during this period. Similar decreases in atomic N/P in the near surface sections of the cores were also observed at the other sites, but over different time frames (*e.g.* after 1984 at Russell Key, after 1982 at Bob Allen Keys, and after about 1970 at Whipray Basin). Downcore changes in atomic N/P below this near surface zone at all sites were driven largely by changes (increases and decreases) in the total N content of the sediments. These downcore changes were most pronounced at Russell Key and Whipray Basin (Figure 8).

Geochemistry of Seagrass Fragments

Living seagrass (*Thalassia testudinum*) and seagrass fragments from the coarse fraction of sediment (visually identified as *Thalassia testudinum*) from Pass Key and Bob Allen Keys were analyzed for organic C, and total N as described earlier (Figure 9). Living seagrass had organic C contents of 45 and 47% and total N contents of 3.2% and 3.6% at Pass Key and Bob Allen Keys, respectively. These values were considerably higher than those reported by FOURQUREAN *et al.* (1992) for *Thalassia testudinum* from Florida Bay (mean values of 34.6% for organic C and 2.20% for total N). The previous study (FOURQUREAN *et al.,* 1992) used scraping to physically remove carbonates in attached epiphytes from the seagrass, while we used a dilute acid washing treatment (see Analytical Methods). Even a small amount of relatively heavy carbonate left on the grass can greatly alter the results obtained. One explanation for our higher values is that even efficient scraping left a little residual carbonate on the seagrass compared to dilute acid washing. Our atomic C/N values for the living seagrass (15 to 16) were toward the low end of the range of values reported by FOURQUREAN *et al.* (1992):

range of atomic C/N values of 15.7 to 22.8. This was consistent with some residual carbonate left from the physical scraping procedure. Both C and N values would be lowered equally by the additional weight of residual carbonate, but some additional C would be added from the carbonate giving somewhat higher atomic C/N values than those obtained from acid washing. Based on this, we believe dilute acid washing treatment gave more accurate elemental data for the seagrass, although the acid washing treatment may have resulted in some loss of acid labile organic matter from the sample.

Organic C contents of buried seagrass fragments at both sites showed an initial drop to values of about 40% in the top 2 cm of sediment. This likely represented initial loss of labile organic matter after senescence of the seagrass (MACKO *et al.,* 1993). Downcore profiles of organic C at both sites showed little change after this initial loss, with values varying between 38 and 44%. Thus, little additional decomposition of organic C in the seagrass fragments occurred in these highly sulfidic sediments.

In both cores, total N contents of the seagrass fragments initially decreased to values of about 1.2% at about 10 cm, likely due to preferential biodegradation of N-containing organic compounds under anaerobic conditions (MULLER, 1977; ROSENFELD, 1979). After an initial decrease, total N content increased to subsurface values that exceeded those of the living seagrass at these sites (3.7% at Pass Key and 4.5% at Bob Allen Keys). These peak values were observed at about 15 cm at Pass Key and over the range of 15–30 cm at Bob Allen. The observed peaks in total N at about 15 cm in both cores may have resulted from N immobilization, where ammonium or dissolved organic N from porewater is incorporated into the plant fragment (ZIBILSKI, 1987). Dissolved ammonium concentrations in porewater were nearly 400 μM at Pass Key and 60 μM at Bob Allen (OREM, unpublished data). The porewater dissolved ammonium profiles at both sites showed distinct maximum concentrations at depth (OREM, unpublished data), but the maxima did not correlate with maxima observed in the total N contents of the seagrass fragments.

Another explanation of the downcore peaks in the total N content of the seagrass fragments is that they reflected historical changes in the N available to the seagrass for assimilation. Previous work had shown that the C:N:P ratio of seagrass leaves changed in response to the available nutrients in the surface water (FOURQUREAN *et al.,* 1992). If this hypothesis is valid, then peaks in the available nitrogen for seagrass at Pass Key occurred about 1960 (base of core), and in the mid to late 1980's, with a peak around 1989 (Figure 9). At Bob Allen, peaks in available nitrogen occurred about 1924, from about the mid 1950's to the late 1960's, in 1976, and in 1992. The subsurface peaks in total N in the seagrass fragments roughly corresponded to periods of increased total N content in the profiles of the fine sediment fraction from these sites: after 1980 at Pass Key and after 1950 at Bob Allen (compare Figures 4 and 9). There were, however, some discrepancies between the total N profiles of the seagrass fragments and the fine sediment fraction. For example, the peak in total N observed in the seagrass fragments in 1960 at Pass Key was not observed in the fine sediment, and the peak in total N in the seagrass fragments in 1924 at Bob Allen was recorded earlier (1912) in the fine sediment fraction.

The atomic C/N ratios of the buried seagrass fragments at the Pass Key and Bob Allen Keys sites are also shown in Figure 9. Because of the relative invariance of the organic C profile downcore at both sites, the C/N downcore plots generally resembled mirror images of the total N profiles.

Stable Isotope Analysis

Stable isotope results ($\delta^{13}C$ and $\delta^{15}N$) for living seagrass, seagrass fragments, and the organic matter in the fine fraction of sediments from Pass Key and Bob Allen Keys are presented in Figure 10. The $\delta^{13}C$ values for the living seagrass were -9.1 permil and -8.5 permil for Pass Key and Bob Allen, respectively. The somewhat lighter values from Pass Key may have reflected its proximity to runoff from the lower Everglades compared to the more marine Bob Allen site (FOGEL and CIFUENTES, 1993). The $\delta^{15}N$ values were also slightly heavier at the Pass Key site (5.9 permil), compared to Bob Allen (5.3 permil). Again, this likely reflected the proximity of the Pass Key site to terrestrial runoff (FOGEL and CIFUENTES, 1993).

The downcore profiles of $\delta^{13}C$ for buried seagrass fragments and the fine fraction of the sediment paralleled each other, but the values for the fine sediment fraction were lower (*i.e.* isotopically lighter) by 4.7 to 7.5 permil at Pass Key, and 3.2 to 5.2 permil at Bob Allen. These differences reflected the contribution of organic C from ^{13}C depleted (isotopically lighter) algae to the organic matter in the fine sediment fraction (FOGEL and CIFUENTES, 1993). Only small variations were observed in the downcore $\delta^{13}C$ values of buried seagrass fragments and fine sediment at both sites. At Pass Key, the buried seagrass fragments showed a gradual increase in $\delta^{13}C$ with depth to 55 cm (1969). This trend likely represents slow biodegradation of isotopically lighter organic matter under anaerobic conditions in the sediments (MACKO *et al.,* 1993). Below 55 cm the $\delta^{13}C$ values of the seagrass fragments decreased by 2.8 permil, suggesting a possibly shift to more terrestrial input (*i.e.* increased freshwater runoff). Notably, this was the approximate period of canal construction in the Taylor Slough region (C111 canal), which resulted in diminished freshwater runoff to Florida Bay (LIGHT and DINEEN, 1994). The $\delta^{13}C$ values of the fine sediment fraction from Pass Key showed little change in the downcore profile, except for a bulge of somewhat heavier values between 1987 and 1995. The timing of this corresponded to increased deposition of C, N, and P to the sediments at this site discussed earlier. Increased algal productivity in the water column at this site during this time period would account for the observed isotopic shift to slightly heavier values. At Bob Allen, $\delta^{13}C$ values of both the buried seagrass fragments and the fine sediment fraction showed a gradual increase with depth, probably reflecting biodegradation of the isotopically lighter fractions of the available organic C, leaving the residual sedimentary organic C heavier by mass balance.

The $\delta^{15}N$ values of the fine sediment fraction from the Pass Key core varied over a relatively narrow range, 5.5 to 4.4

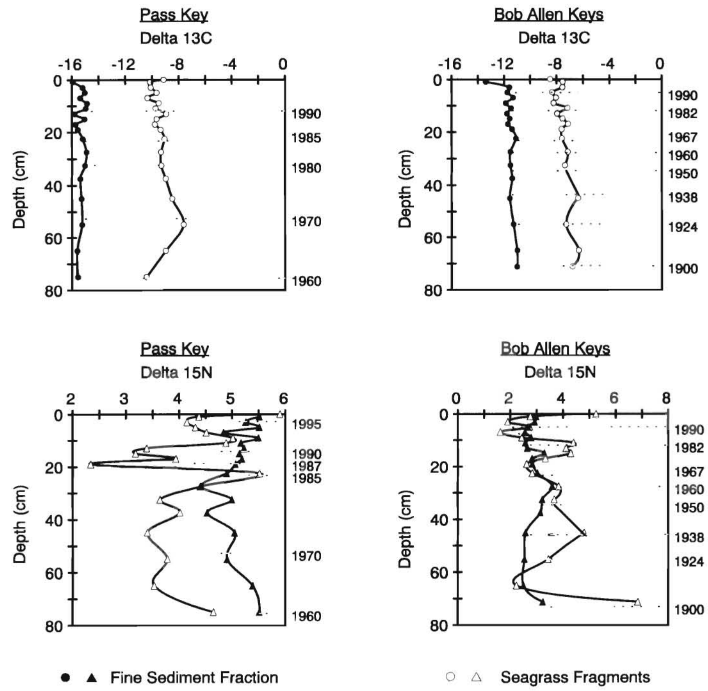

Figure 10. Stable isotope data ($\delta^{13}C$ and $\delta^{15}N$) for buried *Thalassia testudinum* fragments, and organic C and total N in the fine sediment fraction from the Pass Key and Bob Allen Keys sites in Florida Bay.

permil (Figure 10). The depth profile of the fines for this core showed a gradual decrease with depth in $\delta^{15}N$ of about 1.5 permil to 27.5 cm (1983), and then a gradual increase of about 1.5 permil to the bottom of the core (1960). Biodegradation typically involves bacterial utilization of the lighter fraction of organic nitrogen leaving the heavier nitrogen behind in the sediments. This produces a vertical profile of increasing $\delta^{15}N$ with depth (MACKO *et al.,* 1993). This behavior was observed below about 27.5 cm at the Pass Key site (*i.e.* before 1983). The $\delta^{15}N$ profile after 1983, however, suggested that a shift to a source of N with heavier overall $\delta^{15}N$ values had occurred; possibly increased algal input to the sediments, since algae have somewhat heavier $\delta^{15}N$ values compared to terrestrial plants (FOGEL and CIFUENTES, 1993). Elemental C, N and P data were also consistent with increased algal input to the sediments at Pass Key since the mid 1980's, as discussed earlier. At Bob Allen, the $\delta^{15}N$ values of the fines also varied over a narrow range (2.5 to 3.3 permil), but with lower values compared to those at Pass Key. This likely reflected differences in the sources of N at Pass Key and Bob Allen (a farther offshore site); possibly a greater influence of N from seagrass at Bob Allen. The $\delta^{15}N$ values of the fines from Bob Allen showed little change downcore, but had a peak around 1960. The increase from the surface to a peak $\delta^{15}N$ value at 27.5 cm (1960) at Bob Allen may have resulted from: (1) preferential biodegradation of lighter N, or (2) somewhat more input from algae in 1960 compared to the present.

The $\delta^{15}N$ values for the living seagrass were similar at both sites: 5.9 permil at Pass Key and 5.3 permil at Bob Allen. The downcore $\delta^{15}N$ profiles for the seagrass fragments were somewhat erratic at both sites, with no discernable trends (Figure 10). The ranges of $\delta^{15}N$ values in the seagrass fragments from the two cores were similar at both sites; between 2 and 5 permil for most samples. In contrast, the $\delta^{15}N$ values of the fine sediment fraction were significantly heavier at Pass Key compared to Bob Allen. One explanation for this discrepancy is that seagrass may obtain much of its N from porewater (recycled N) rather than from surface water as algae does (algae being the major contributor to N in the fine sediments). This would essentially buffer the seagrass from changes in the source of N to surface water. Another potential factor is that biodegradation of N-containing organic compounds in seagrass fragments may be different than biodegradation of bulk organic matter in the fine sediments. A larger set of N isotope data will be needed before more detailed conclusions on the N dynamics in Florida Bay can be drawn.

CONCLUSIONS

Our interpretation of results from this study suggested that recent nutrification (*i.e.* increases in the N and P load to sediments) occurred in portions of eastern and central Florida Bay, beginning in the early to mid 1980's at most sites. This was indicated by sudden and sometimes dramatic shifts in the concentrations of organic C, total N, and total P, and the atomic C/N and C/P ratios of sediments in the near surface sections of cores collected at the five sampling sites established for this study (Figures 3–7). The magnitude of the shifts were in excess of what would be expected from normal diagenetic processes, and the shapes of the downcore profiles also suggested that the effect was source related and not diagenetic. The observed nutrification was most pronounced at Pass Key located in the northeastern portion of the bay (closest to terrestrial input), and least pronounced at Bob Allen Keys, the most southerly area (most marine influence), (Figure 1). Enhanced concentrations of both N and P were observed, but the effect appeared to be significantly greater for P. At Pass Key, the sediments recorded increased nutrification after 1985, with an earlier nutrification event observed in the mid 1970's. At Russell Key and Bob Allen Keys, recent nutrification was observed to begin about 1982 and 1984, respectively. These dates were consistent within the limits of uncertainty, and point to increased nutrient load (N and P) to eastern Florida Bay in the early to mid 1980's. At the high sedimentation rate, high time resolution Pass Key site, there was also evidence that the recent nutrification switched back to more moderate nutrient levels after 1993. The timing of the observed nutrification directly preceded the first reported observations of microalgal blooms and seagrass dieoff in 1987.

The longer sediment records at the Russell Key and Whipray Basin sites also showed evidence of earlier events of increased nutrient input and enhanced productivity in eastern and central Florida Bay. At Russell Key, an earlier event of increased P input to the sediments was observed during the 1950's. The two cores from Whipray Basin had very similar vertical profiles, with large changes in organic C and total N contents, and moderate changes in total P concentrations of the sediments recorded downcore. The similarity of the profiles from the two Whipray sites located in the NE and SW sections of the basin suggests that the processes controlling changes in C, N, and P downcore acted across the entire basin. A very large productivity event is recorded from about 1730 to 1800; peaks in organic C and total N dated at 1741 nearly equaled surface sediment concentrations. Another, somewhat smaller peak in organic C and total N was recorded from about 1850 to 1900 at the two Whipray sites. The decadal scale of these events suggested that they were not the result of isolated events such as hurricanes, but were caused by longer scale changes in the environment such as shifts in water circulation in the bay, or changes in rainfall patterns. The timing of the mid 1700's peaks in organic C and total N in Whipray Basin during the height of the "Little Ice Age", corresponded to a period of cooler temperatures in the Florida Straits (DRUFFEL, 1982), and probable deeper water (increased rainfall) in the freshwater Everglades to the north (WILLARD *et al.,* 1999; WEIMER, 1998). We speculate that the increased rainfall during this cooler period resulted in greater discharge of freshwater and N load to central Florida Bay from Taylor Slough and possibly Shark River Slough. This, in turn, would have stimulated productivity in the bay during the mid 1700's. Surprisingly, these historical peaks in organic C and total N were periods of relatively low or moderate total P concentrations. An historical peak in total P was observed between about 1800 and 1850 in Whipray Basin, but this did not correspond to any concomitant peaks in the organic C or total N data. This suggested that the Whipray Basin area had historically been limited more by N than by P. The two Whipray Basin cores also recorded recent nutrification beginning about 1947, with significant increases in organic C, total N, and total P.

The $\delta^{15}N$ results from Pass Key (Figure 10) also suggested that changes in the nutrient regime occurred here beginning in the early 1980's. The trend in the $\delta^{15}N$ data at Pass Key from 1980 to 1996 (a change to heavier values at the surface) suggested a shift in the source of N to this site during this period. Differences in the $\delta^{13}C$ values of seagrass fragments and organic matter in the fine sediment fraction between Pass Key and Bob Allen Keys suggested more terrestrial sources of C at Pass Key and more marine sources at Bob Allen. This was consistent with their geographic locations (Figure 1).

The results of the analysis of cores from adjacent seagrass-covered and barren areas showed that, near the surface, barren areas had distinctly lower organic C, total N, and total P, and were generally finer-grained compared to seagrass-covered areas. At depth, however, the sediment size and chemical composition (organic C, total N, and total P) of sediments from barren and seagrass-covered areas were generally similar. It was also observed that barren areas contained abundant seagrass fragments below the surface. We concluded from this that the barren areas were formerly covered with seagrass, but have been buried by relict sediment moved to the site by physical processes in the estuary. The sediment size data and some of the chemical data at the Whipray basin NE site (currently seagrass-covered) suggested that the process of burial may be occurring there at present. The Whipray NE site may, therefore, represent a favorable location for studies of the processes involved in the burial of seagrass beds.

Studies of sediment geochemistry can provide useful information on the history and dynamics of environmentally important elements in the Florida Bay ecosystem, such as C, N, and P. We are currently examining cores from these same sites in order to replicate the results presented here, and to increase the time resolution. Organic biomarker studies are also being conducted to examine the nature of the historical productivity maxima observed in Whipray Basin during the height of the "Little Ice Age" in the mid 1700's.

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