IMPINGEMENT OF ORGANIC-RICH, CONTAMINATED SEDIMENTS ON MANATEE POCKET, FLORIDA

JOHN H. TREFRY, NAI-CHI CHEN, ROBERT P. TROCINE AND SIMONE METZ

Department of Oceanography, Ocean Engineering and Environmental Science
Florida Institute of Technology, Melbourne, Florida 32901

ABSTRACT: *Fine-grained, organic-rich sediments are adversely impacting portions of the coastal zone in Florida. One extreme example is found in Manatee Pocket, on the southeastern coast of Florida, where sediments with >4% organic carbon have an average thickness of about 1 m and a total volume of 340,000 m³. These deposits formed as soil and organic matter were carried into Manatee Pocket and trapped during the past 100 years of regional development. Vertical profiles for Cd, Cu, Hg, Pb, and Zn show that contamination, at 5-10 times above natural levels, is restricted to the top 15-30% of the organic-rich layers of sediment. Thus, despite a long history of sedimentation problems, incoming sediments have been burdened with contaminants only since the 1950s.*

COASTAL waterways in Florida and worldwide are being stressed by inputs of fine-grained, organic-rich sediment (Fernald and Patton, 1984; Trefry et al., 1990). One common stress is depletion of oxygen in sediments and bottom water as the result of decaying organic matter. Benthic habitats are altered when the natural sandy substrate is covered with a black, fine-grained, sediment ooze. In addition, resuspension of such sediments increases turbidity and inhibits light penetration leading to a decline in the growth of seagrasses. Finally, contaminants are effectively adsorbed and stored by this high surface area material.

One noteworthy site of impact in Florida is Manatee Pocket, where large amounts of fine-grained, organic-rich sediment have been trapped. Manatee Pocket is part of the St. Lucie Estuary and is located near the confluence of the estuary with the Indian River Lagoon and the Atlantic Ocean (Fig. 1). Water depths in the pocket are typically 1-2 m and salinities range from <1‰ in adjacent creeks to >30‰ throughout much of the embayment. Available data for surficial sediments show elevated levels of Cd, Cu, Hg, Pb, Zn, chlordane, and PCBs (Davis, 1987; Haunert, 1988). More detailed knowledge of the vertical and horizontal distribution and magnitude of contamination is required to plan pollution prevention and remediation strategies.

METHODS—Field sampling in Manatee Pocket was carried out during April 6 and 7, 1989 using a small, shallow-draft vessel. Twelve sediment cores were collected, eight with a Benthos gravity corer and four with a vibra corer. Each core penetrated through fine-grained, organic-rich sediment to sand or shell. Core lengths ranged from 19-204 cm, averaging 122 cm. Each core was split longitudinally to describe sediment lithology and then subsectioned into 1-cm intervals over the top 10 cm and 2- to 5-cm thick layers below 10 cm. Surficial sediments (top 2 cm) were collected by a diver at 21 locations (Fig. 1). All sediment samples were placed into tared plastic vials, weighed, freeze-dried, and then reweighed to determine water content. A small portion of each sample was saved wet for Hg analysis.

Total concentrations of Al, Cd, Cu, Fe, Pb, and Zn in sediments were determined by atomic
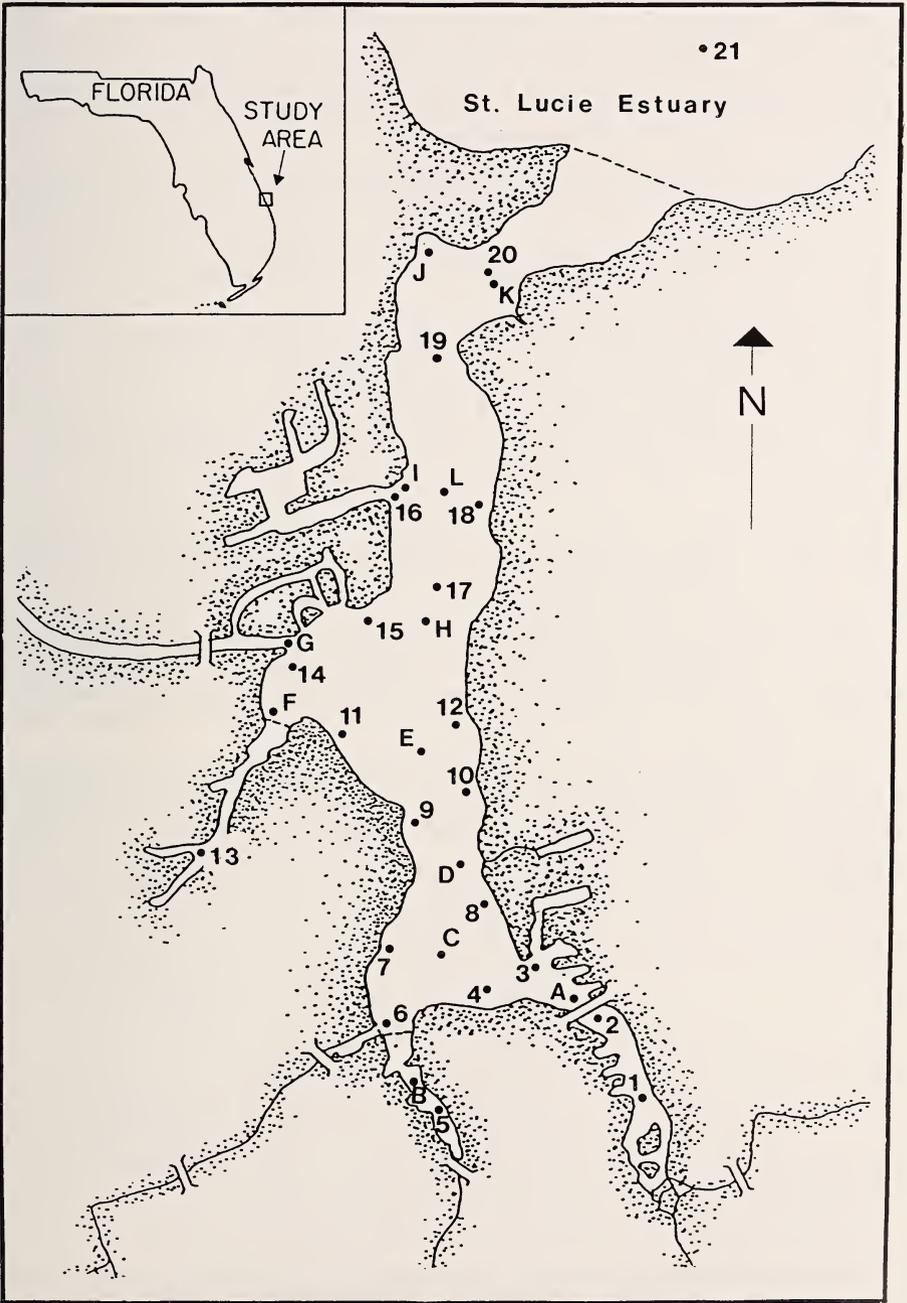
Fig. 1. Map showing sampling stations for Manatee Pocket with inset map identifying site location on the southeastern coast of Florida. Numbers identify locations of surface grab samples and letters show core sites.

absorption spectrophotometry (AAS) following complete digestion of 0.4 g samples using HNO_3-HF-$HClO_4$ in Teflon beakers fitted with Teflon watch covers as described in Trefry and Metz (1984). Sediment solutions and reagent blanks were analyzed using a Perkin-Elmer model 4000 instrument equipped with deuterium and tungsten background correction as well as an HGA-400 heated graphite atomizer and an AS-40 autosampler. Concentrations of Al, Cu, Fe, and Zn were determined by flame AAS and values for Cd and Pb were obtained using heated graphite atomization.

Sediment Hg values were determined by heating separate 2-g aliquots of sediment with 5 mL of concentrated, redistilled HNO_3 in a 65°C water bath for 1 hour. The reaction was carried out in acid-washed, polypropylene centrifuge tubes. After heating, the samples were cooled to room temperature, centrifuged, transferred to a graduated cylinder, and diluted to a final volume of 25 mL with distilled, deionized water. Analyses were carried out by cold-vapor AAS using a Laboratory Data Control Mercury Monitor.

Concentrations of total organic carbon, total nitrogen, and total sulfur were determined using a Carlo-Erba NA1500 nitrogen/carbon/sulfur analyzer. Samples were acidified with HCl to drive off inorganic carbon and dried in an oven at 70°C. The concentrations of C, N, and S were determined following combustion of 10-mg samples in tin cups at 1000°C. The carbonate content of the sediments was measured using the gasometric technique of Schink and co-workers (1978). Silicon concentrations were determined on separate aliquots of sediment following digestion in sealed Teflon tubes to prevent volatilization and loss of Si as SiF_4. Analysis followed by flame AAS.

Analytical precision was determined using replicate samples and was better than 10% for each element. Accuracy was determined by analysis of certified standard reference materials (SRM) available from the National Institute of Standards and Technology (NIST) and the National Research Council of Canada (Table 1).

Sediment accumulation rates and age determinations were measured by Pb-210 and Cs-137 geochronologies. The gamma activities of Pb-210 at 46.5 keV, Pb-214 at 351.8 keV, and Cs-137 at 661.6 keV were determined using a Princeton Gamma-Tech intrinsic germanium detector (Cutshall et al., 1983). Counting efficiencies and accuracy were determined by analyzing SRM 4350B, an NIST sediment sample calibrated for environmental radioactivity, and samples from Manatee Pocket that were spiked with Pb-210 and Cs-137.

TABLE 1. Concentrations for trace metals in Standard Reference Material #1646, an estuarine sediment prepared by the U.S. National Institute for Standards and Technology and for carbon, nitrogen, and sulfur in MESS-1, a marine sediment prepared by the National Research Council of Canada.

Element	Certified Concentration	This Study (n=10)
Al	6.25 ± 0.20%	6.18 ± 0.07%
Cd	0.35 ± 0.07 ppm	0.40 ± 0.03 ppm
Cu	18 ± 3 ppm	18.2 ± 0.7 ppm
Fe	3.35 ± 0.10%	3.36 ± 0.06%
Pb	28.2 ± 1.8 ppm	26.2 ± 1.6 ppm
Si	31%°	30.9 ± 0.6%
Hg	63 ± 12 ppb	65 ± 3 ppb
Zn	138 ± 6 ppm	126 ± 4 ppm
C	2.99 ± 0.09%	2.98 ± 0.07%
N	—	0.195 ± 0.003%
S	0.72 ± 0.05%	0.72 ± 0.04%

°Reference concentration.

RESULTS AND DISCUSSION—*Sediment distribution and composition*—The shape and bathymetry of Manatee Pocket (Fig. 1) combine to trap much of the fine-grained material carried in from adjacent creeks and canals. Thus, fine-grained, organic-rich, sediments were found at virtually every site. In this paper, we use the term "muck" loosely to describe black, fine-grained (>60% silt and clay-size particles), organic-rich (>4% organic carbon) sediments with

a high water content (>75% water by weight) (Trefry et al., 1990). McNulty and McNulty (1987) found that the thickness of muck sediments in the pocket varied from 0-259 cm with an average of 135 cm. We found muck sediments extending to depths >200 cm with an average thickness of 84 cm. The larger deposits were generally found in the center of the pocket at deeper water depths where settling and deposition are favored. No muck deposits were found in the adjacent, well-flushed portion of the lower St. Lucie Estuary (Fig. 1).

The total amount of fine-grained, organic-rich sediment in Manatee Pocket was calculated by dividing the area into 63 blocks and using data from our work and that of McNulty and McNulty (1987) for the thickness of organic-rich sediment. These thicknesses were multiplied by the appropriate area to calculate a volume for each block. The total volume of wet, muck sediment for Manatee Pocket is 340,000 m^3. When admixed sand and shell layers are included, this sediment averages about 60% water by weight or 80% water by volume. Thus, the volume of dry sediment is 68,000 m^3 with a mass of 177,000 metric tons (dry density=2.6 g/cm^3). The wet volume of organic-rich sediment for Manatee Pocket is similar to the 270,000 m^3 of wet muck estimated for the Hillsborough River and adjacent river mouth basin in Tampa, Florida (Trefry et al., 1989). This pool of organic matter in Manatee Pocket provides abundant energy for sediment bacterial assemblages to create the observed high sediment oxygen demand that leads to anoxic conditions (Davis, 1987).

Sediments rich in organic carbon persist throughout each core as shown for Station H (Fig. 2). An average of 5.5±3.6% organic carbon was determined for all sediments collected in Manatee Pocket (Table 2). Total nitrogen levels are also high with an overall mean of 0.38±0.22%. The large range in Al, organic carbon, Si, and $CaCO_3$ content of Manatee Pocket sediments (Table 2) results from a mixture of various quantities of clay, organic matter, sand, and shell. Mean values for organic carbon and nitrogen (Table 2) show that the typical sample is rich in organic matter.

Total sulfur concentrations are also high in sediments from Manatee Pocket as shown for Station H (Fig. 2). Overall, S values for all sediments collected averaged 1.9±1.2% (Table 2). An average C/S ratio of 2.5 was found for Manatee Pocket (Table 2), with values >4 for sediment layers containing obvious plant debris and values <1.5 for sand lenses. Berner (1984) reported a C/S ratio of 2.8 as typical for normal marine sediments. This value results from preservation of roughly constant fractions of organic carbon and reduced sulfur with the amount of labile organic matter limiting the production of iron sulfide. Clearly, abundant levels of both organic carbon and reduced sulfur have been preserved in Manatee Pocket sediments (Fig. 2 and Table 2). With such high sulfur loadings throughout these anoxic, sulfate-reducing sediments, remobilization of such metals as Cd, Cu, Fe, and Zn is less likely because the sulfide phases of these metals have very low solubilities.

TABLE 2. Summary of elemental concentrations in sediments from Manatee Pocket, Florida.

| Component | Manatee Pocket | | Average Continental Crust[1] |
	Range	Mean ± S.D.	
C	0.1–28%	5.5 ± 3.6%	—
N	<0.02–1.2%	0.38 ± 0.22%	—
C/N	7–27	14 ± 3	—
S	<0.1–5.5%	1.9 ± 1.2%	—
C/S	0.8–5.9	2.5 ± 1.2	—
$CaCO_3$	<0.2–30%	6 ± 5%	—
Si	11–44%	25 ± 8%	27.7%
Al	0.02–5.1%	2.4 ± 1.1%	8.2%
Fe	0.07–6.0%	2.4 ± 1.2%	4.1%
Cd	<0.01–1.7 ppm	0.25 ± 0.28 ppm	0.11 ppm
Cu	<1–426 ppm	48 ± 86 ppm	50 ppm
Hg	<0.01–17 ppm	0.58 ± 2.2 ppm	0.05 ppm
Pb	<1–100 ppm	22 ± 21 ppm	14 ppm
Zn	0.4–422 ppm	67 ± 92 ppm	75 ppm

[1]Taylor (1964).

Sediment accumulation rates are difficult to determine in shallow water due to non-steady state accumulation, the presence of sand layers and plant debris, as well as physical and biological mixing of sediments. Lower values for organic carbon and total sulfur, nitrogen, iron, and aluminum that appear periodically downcore (Fig. 2) show the presence of sand layers in these cores. Nevertheless, first-order approximations can be made using geochronometers such as Cs-137 and Pb-210.

At Station H, the Cs-137 signal is undetectable below 40 cm (Fig. 2), a depth roughly equivalent to the early 1950s and the start of atmospheric testing of nuclear weapons. Mixing has distorted any clear maximum in Cs-137 activity that might coincide with the 1963 atmospheric maximum input for Cs-137 (Fig. 2). The trend at Station C is similar (Fig. 2) and a sediment accumulation rate of about 1 cm/y is suggested for cores H and C. In contrast, no detectable Cs-137 is found below 20 cm at Station E (Fig. 2) which is consistent with a recent sediment accumulation rate of about 0.5 cm/y.

At Stations H and C, a linear decrease in the natural logarithm (ln) of excess Pb-210 can be followed downcore until the excess Pb-210 signal has decayed away at about 60 and 110 cm, respectively (Fig. 2). Calculated sediment accumulation rates are 0.5 cm/y for Station H and 0.8 cm/y for Station C. These values are slightly lower than determined from the Cs-137 profiles, suggesting that mixing has somewhat shifted isotope distributions. The presence of various sand and shell layers for Station E and only a short linear trend in excess Pb-210 make accumulation rates by Pb-210 unreliable for this core. Sediments at depths >100 cm in Manatee Pocket most likely date back into the late 1800s. However, we cannot calculate the absolute ages of the oldest sediments because they extend beyond the 100-120 year range of our techniques. Although only speculative at this time, the deeper muck layers represent either long-term natural runoff of organic-rich sediments or a large pulse of natural, organic-rich sediment sometime during the late 1800s.
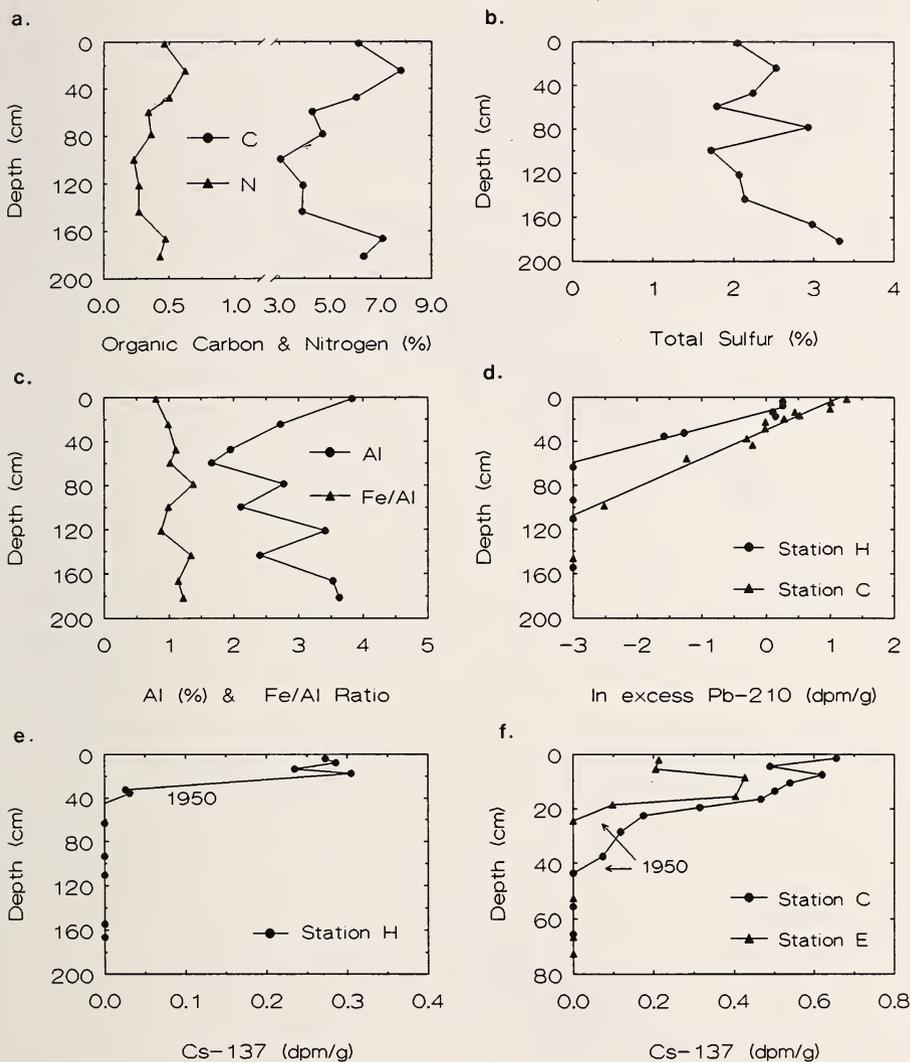
FIG. 2. Vertical profiles of (a) organic carbon and total nitrogen for Station H, (b) total sulfur for Station H, (c) Al and the Fe/Al ratio for Station H, (d) ln excess Pb-210 for sediment cores from Stations H and C, (e) Cs-137 for Station H, and (f) Cs-137 for Stations C and E.

Trace metal contaminants—Concentrations of Al, Cd, Cu, Fe, Hg, Pb, and Zn in surficial sediments from Manatee Pocket vary considerably (Table 2). Lowest values are associated with sandy sediments whereas higher values are typically found with fine-grained, muck deposits. The reasonably good correlation between Fe and Al (Fig. 3) results because both metals are associated with fine-grained aluminosilicate minerals. Iron may be present as a structural component of the aluminosilicates, as an oxide coating, or as a separate sulfide phase. A good correlation also was observed for Fe versus S (Fig. 3).
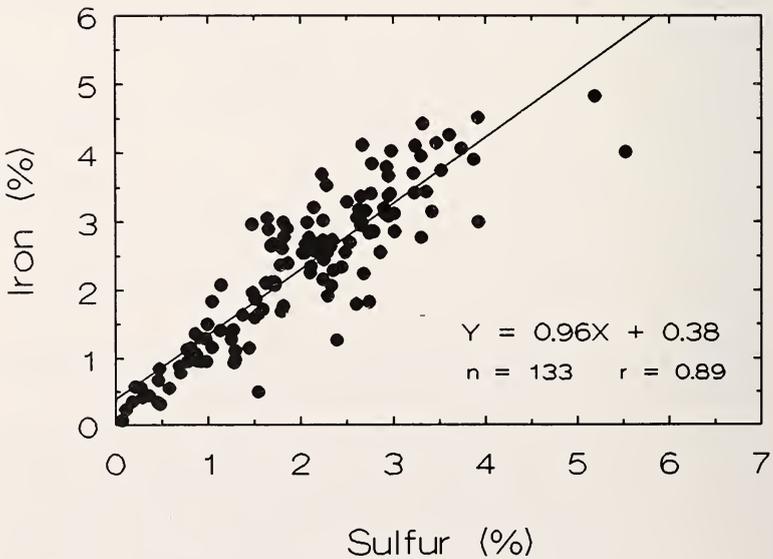
a.

$Y = 0.85X + 0.32$
$n = 146 \quad r = 0.82$

b.

$Y = 0.96X + 0.38$
$n = 133 \quad r = 0.89$
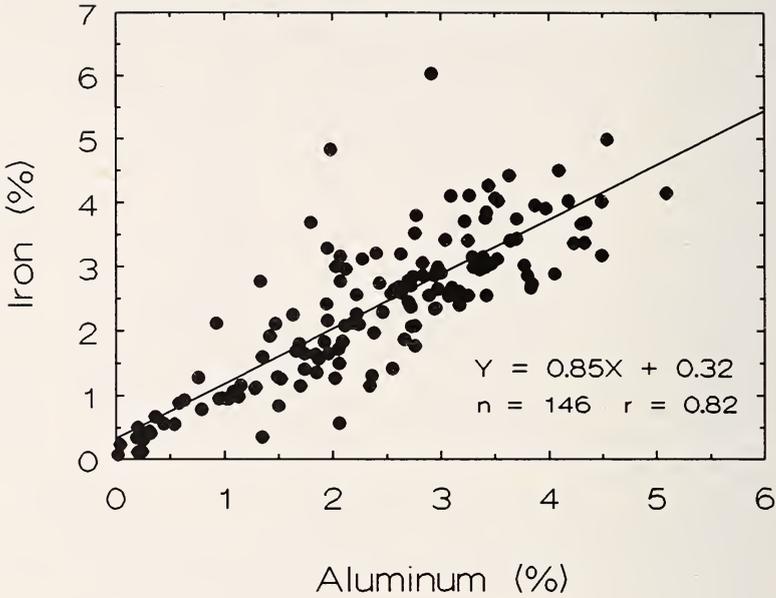
FIG. 3. Scatter plots showing (a) total iron versus total aluminum; and (b) total iron versus total sulfur for sediment samples from Manatee Pocket.

Such overall good correlations among Al, Fe, organic carbon and S occur because contributions of terrestrial organic carbon are accompanied by higher concentrations of Fe and Al in continental detritus (Middelburg, 1991). Furthermore, diagenetic reactions controlled by the decomposition of organic carbon directly influence the reduction of sulfate to sulfide and the formation of abundant iron sulfides.

Under natural conditions, concentrations of many trace metals correlate well with Al and Fe because they too have a strong affinity for fine-grained aluminosilicates. In addition, Al, Fe, and most trace metals are not abundant in quartz sand, carbonate, and most estuarine organic matter; thus, total aluminum and iron concentrations provide a means for normalizing other sediment metal values (Bruland et al., 1974; Trefry and Presley, 1976). Within the State of Florida, Schropp and co-workers (1990) have adopted these approaches to identify metal contamination in sediments.

Sediments are considered to be contaminated with Cu when values for the Cu/Al ratio are greater than background levels and above the 95% prediction interval for the natural Cu/Al ratio (Fig. 4). Nineteen of the 21 surface samples from Manatee Pocket and many of the subsurface samples are contaminated with Cu based on the Florida guidelines. The trend for Hg is similar to that for Cu. All surficial sediments from Manatee Pocket have Pb (Fig. 4) and Zn concentrations that are greater than natural levels based on Pb/Al or Zn/Al ratios.

The historical influx of trace metals was evaluated along a south-north transect across Manatee Pocket as well as downcore by focusing on sites C, E, H, L, and K (Fig. 1). Organic carbon values exceed 4% throughout all of these cores, except in sandy sediments at Station K near the mouth of Manatee Pocket. Highest Zn concentrations are found in the southern end of Manatee Pocket (Station C), with an overall decrease toward the mouth (Fig. 5). A similar spatial distribution was observed for Hg (Fig. 5) and other metals. This trend is consistent with a source of trace metals in upland areas with transport through the main creeks to Manatee Pocket.

Zinc concentrations and Zn/Al ratios are above natural levels in the top 20-60 cm at sites C, E, H, and L (Fig. 5). In deeper sediment layers, background Zn levels and Zn/Al ratios are observed (Fig. 5). It is unlikely that surface enrichment of metals is related to remobilization of the metals in subsurface sediments followed by upward transport and deposition of metals in surficial layers because the total sulfur content is high throughout the core. The onset of Zn contamination is also consistent from site to site. For example, at Stations C and H, elevated Zn levels can be traced to about 40 cm, or the early 1950s. At Station E, the 1950 horizon is at about 20 cm due to a slower rate of sediment accumulation.

The vertical trends described for Zn are similar for Cu, Cd, Hg (Fig. 5), and Pb. Deeper, pre-1950s sediment has natural metal levels, indicating that 70-85% of the total muck is uncontaminated. When metal levels are elevated, the degree of contamination exceeds natural levels by a factor of 5-10. An
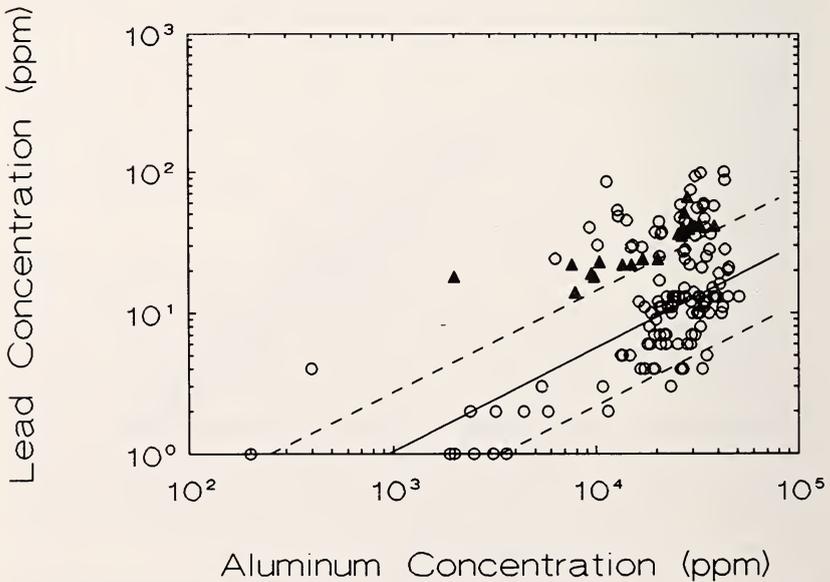
a.
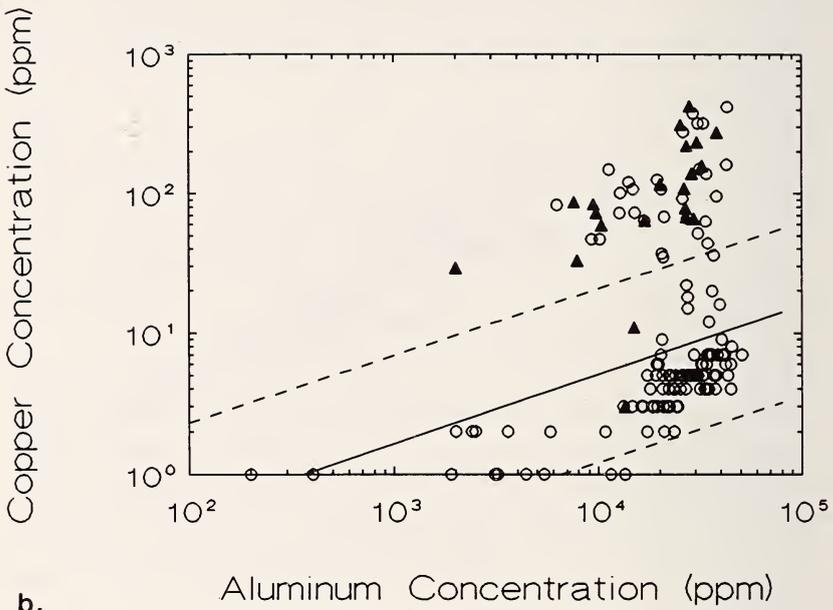
b.

Fig. 4. Scatter plots showing (a) total copper versus total aluminum; and (b) total lead versus total aluminum for sediments from Manatee Pocket. Triangles identify values for surficial sediments (0-2 cm) and open circles show data for subsurface sediments. Solid line shows the linear regression and dashed lines identify 95% prediction intervals.
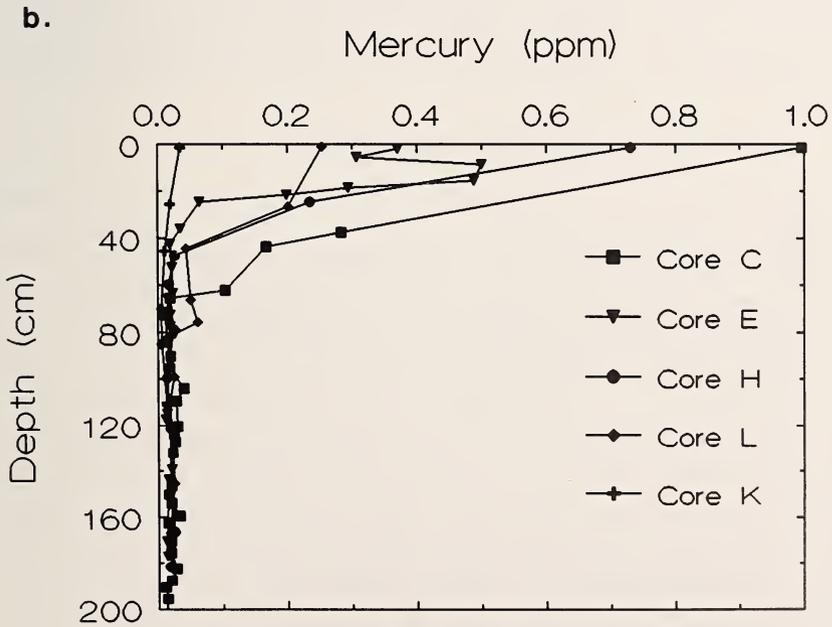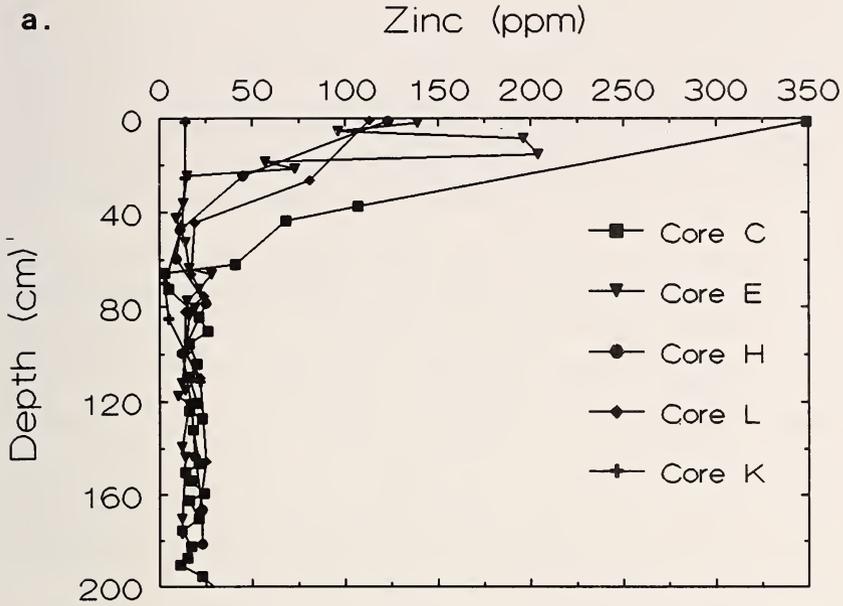
a.

b.

Fig. 5. Vertical profiles for (a) total zinc and (b) total mercury in sediments from Stations C, E, H, L, and K.

exception to the above trend occurs at core site B where concentrations of Hg in the sediments were as high as 17 ppm, at least 200 times greater than natural levels. This incidence of Hg contamination persisted at levels >5 ppm to a depth of 35 cm. No other site has Hg contamination to the same extent, suggesting that the southwest prong of Manatee Pocket is a potential source area. The vertical extent of contamination for Cu, Hg, and Cd is slightly deeper than that for Zn and Pb and suggests that inputs began somewhat before the 1950s.

CONCLUSIONS—Fine-grained, organic-rich, sediments were found at virtually every site in Manatee Pocket. The shape and bathymetry of the pocket effectively trap fine-grained material. Concentrations of organic carbon were as high as 9% with sediments containing >4% organic carbon extending to depths of 100-200 cm in many areas. Vertical profiles for trace metals show contaminant levels only in the top 20-60 cm, which is equivalent to 15-30% of the total length of the muck layer. Thus, a layer of metal-contaminated muck overlies a larger uncontaminated layer. The onset of metal contamination dates to the 1950s for Pb and Zn and somewhat earlier for Cd, Cu and Hg. Prior to the past 40 years, fine-grained, organic-rich sediment accumulated in Manatee Pocket, but without its present-day metal burden.

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