Estuarine Research Federation

The Historical Record of Metal Enrichment in Two Florida Estuaries

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ABSTRACT: Historical profiles of metal accumulation have been generated for the lower St. Johns River and Hillsborough Bay, Florida, in cores representing approximately 50 yr of sediment and metal accumulation. These profiles demonstrate that Cd, Pb, and Zn are enriched in these Florida estuarine sediments. Pb enrichment has decreased since the mid 1970s because of reduced use of leaded gasoline. In the St. Johns River, most metals exhibit a trend of increasing enrichment with time. Cd enrichment significantly decreased between 1970 and 1975 as a result of reduced discharges into the river and control of aquatic vegetation. In Hillsborough Bay, enrichment factors for most metals are relatively high and show little change downcore. Cr, Cu, and Ni border on enrichment and Pb, Cd, and Zn are enriched. The results of this study are consistent with other studies of surficial-sediment metal concentration in other Florida estuaries.

Introduction

Metal contamination of the coastal zone is becoming a significant concern as development extends into once-pristine areas. Spatial surveys of surficial-sediment metal concentration are the first step in evaluating this problem in a given area. Subsequent determination of the temporal record of metal accumulation can indicate contamination sources and the effectiveness of existing efforts at controlling contaminant input. However, well-constrained, temporal history studies are rare (e.g., Bruland et al. 1974). This study examines the historical record of metal enrichment in St. Johns River and Hillsborough Bay, Florida (Fig. 1A and 1B).

Identifying areas of metal contamination is not a straightforward task. Metals occur naturally in sediments and thus have both a natural and an anthropogenic signal. These natural concentrations cause further difficulty because background values vary greatly between different source regions and with changes in grain size and mineralogy (Turekian and Wedepohl 1961; Wong and Moy 1984). Numerous methodologies have been employed to correct for these factors, with the result that most previous studies are site-specific and cannot easily be compared with other areas within a given region (see, for example, Mayer and Fink 1980; Klinkhammer and Bender 1981; Ackermann et al. 1983; Trefry et al. 1985; Stoffers et al. 1986). Because of the wide range of siliciclastic and carbonate sediments present on the Florida peninsula, correction for size and source variations is particularly important in the interpretation of metal concentrations.

Normalization to aluminum as a reference element is a successful technique that has been employed by numerous authors to correct for variations in composition and grain size (e.g., Goldberg et al. 1979; Klinkhammer and Bender 1981; Tre-

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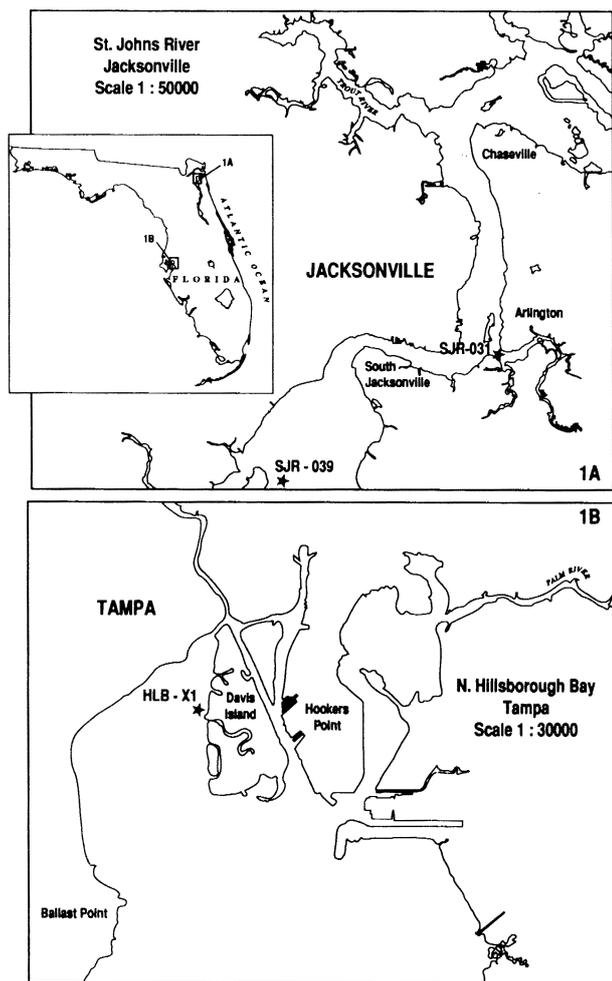
Fig. 1.   Maps showing the location of cores collected for this study. Location of the two study areas shown on inset Florida map. Cores analyzed for Pb-210 geochronology shown by a star and station designation. A) St. Johns River (cores SJR-039 and SJR-031). B) Hillsborough Bay (core HLB-X1).

fry et al. 1985; Schropp et al. 1990). Aluminum as a normalizer has the advantage of being representative of the quantity of aluminosilicates (the most important carrier phase of adsorbed metals) and thus serves to compensate for both grain-size and mineralogical variation (Windom et al. 1989). Aluminum normalization allows comparison of sediment metal concentrations on a regional basis when these measurements are combined with a regional database of metal concentrations in uncontaminated sediments. Such a database has been developed for the Florida and Georgia coasts (Windom et al. 1989; Schropp et al. 1990). This database of over 450 samples demonstrates that metal concentration and aluminum content are well correlated, that aluminum is a useful reference element for this region, and that comparison between study sites within this region is possible. This database

has been used successfully to evaluate the extent of surficial sediment contamination in Florida bays and estuaries (Schroppe et al. 1990). Previous historical studies of sediment contamination have assumed a background metal concentration from core-bottom values against which to compare more modern concentrations (e.g., Goldberg et al. 1979; Trefry et al. 1985). The database developed by Windom et al. (1989) and Schropp et al. (1990) provides quantitative values for uncontaminated sediment concentrations for a given aluminum concentration and thus should allow a better estimate of anthropogenic inputs. In areas where sediment accumulation is rapid and pre-industrial metal concentrations are not reached in a core, accurate interpretation of enrichment factors cannot be made without the use of a regional database to provide metal concentration values for uncontaminated sediments.

Study Areas

Coring locations were chosen based on the presence of fine-grained sediment and proximity to urban areas. Soon after core collection, X-radiographs of the cores were made and were used to identify the subset of cores that exhibited laminated sedimentary structure, which could provide an undisturbed record of metal accumulation.

The St. Johns River, the longest river in Florida, is a coastal plain river that rises in the low freshwater marshes in the central and northeastern portion of the state (Fig. 1A). The river is shallow and drops only 8 m along its 440 km length (DeMort 1991). Because of this low gradient, daily tidal reversals occur up to 160 km inland from the river mouth. Tidal flows are significantly greater than the freshwater flow, reducing the flushing capacity and increasing the retention of pollutants in the river. Two cores (SJR-039 and SJR-031) from the Jacksonville area were analyzed for Pb-210 geochronology. Salinities and water depths were 14‰ and 6.5 m (SJR-039) and 20 ‰ and 2.0 m (SJR-031) for these two cores.

Hillsborough Bay is the uppermost northeastern section of Tampa Bay (Fig. 1B). Recent work compiled by Long et al. (1991) documents that of the subregions in Tampa Bay, Hillsborough Bay ranks first in contamination of most metals (Cd, Cr, Cu, Hg, Pb, Zn). Sediments in upper Hillsborough Bay are >50% silt and clay; in our study area this percentage increases to 95–100% (Doyle et al. 1989). Core HLB-X1 was collected in 3.5 m of water adjacent to and west of Davis Island. Dredging associated with the Port of Tampa has significantly altered the sedimentary environment in the bay (Fehring 1985), making it difficult to collect undisturbed cores in other parts of Hillsborough Bay.

Laboratory and Field Methods

A total of 11 cores (eight from Hillsborough Bay and three from St. Johns River) were collected in 1990. Cores for radiochemical and trace-element analyses and contiguous slabs for X-radiography were collected by divers in open-barrel PVC core tubes (50 cm long, 15 cm dia.) and in plexiglass trays (40 cm × 12 cm × 2.5 cm, LWH), respectively. The large diameter of the core barrel minimized compaction and disturbance that may be associated with coring operations. X-radiographs were produced with a Faxitron portable x-ray unit immediately upon return to shore. Cores selected for radiochemical and trace-metal analyses were extruded and subsampled at 1-cm intervals. Subsampling occurred typically within a few hours of core collection. Samples for trace-metal analyses were removed from the center of each interval to guard against contamination from wall effects and were frozen immediately. The bulk of each interval was packed in a plastic bag for radiochemical analysis.

Sediment samples for analysis of Al, As, Cd, Cr, Cu, Pb, Ni, and Zn were totally digested in a combination of high purity (Baker Instra-Analyzed) nitric, perchloric, and hydrofluoric acids. Typically, 250 mg of sediment was placed in a Teflon beaker along with 10 ml each of HF and HNO_3 to form silicon tetrafluoride, which was driven off overnight at low heat. Subsequently, 3 ml of $HClO_4$ were added to remove organic matter. The samples were taken to dryness at temperatures not exceeding 150°C, and the residue was redissolved in 1% HNO_3 to remove chlorides present from the $HClO_4$ digestion. These chlorides create a number of isobaric interferences in ICP/MS analyses. Each set of digestions included at least two reagent blanks and two certified reference standards such as the NBS standard reference material #1646. Accuracy of the metals determination was 90% for Al, As, Cr, and Zn, 92% for Ni, and 95% for Cu and Pb; precision was ± 10%.

Enrichment factors relative to uncontaminated sediments were calculated as described in Schropp et al. (1990). Their study measured concentrations of Al, As, Cd, Cr, Cu, Pb, Ni, and Zn in uncontaminated Florida estuarine sediments to construct regression plots of metal vs. aluminum concentration. These regression equations allowed us to calculate expected metal concentrations in the absence of contamination for a given aluminum concentration. The concentration of each metal measured in this study was compared to the concentration predicted by the upper 95% confidence interval boundary around the regression line for the uncontaminated sediments. By employing a higher threshold value for uncontaminated metal concentrations, this study determined enrichment and trends in metal concentrations with high statistical significance.

Total carbonate was measured by weight difference between acidified and unacidified samples (Carver 1971). Total organic carbon and total nitrogen were analyzed on a carbonate-free basis (using the residue from the total carbonate analysis) with a Perkin Elmer Model 240C elemental analyzer. Accuracy and precision of the organic carbon and nitrogen analyses were 95% and ± 10%, respectively.

Radionuclide activities were determined using a low-background, planar germanium detector, a computer-based, multichannel analyzer, and the ORTEC MAESTRO gamma-analysis software. Total Pb-210 activity was directly determined by measurement of its 46.5 KeV gamma peak in dried, homogenized sediment (Cutshall et al. 1983). The supported level of Pb-210 from the decay of Ra-226 was determined for each depth interval by concurrently measuring the gamma activity of Pb-214 (at 295 KeV and 352 KeV) and of Bi-214 (at 609 KeV), the short-lived granddaughters of Ra-226. Cs-137 activity was directly determined by measurement of its 661.6 KeV gamma peak in dry, homogenized sediment (Kuehl et al. 1986). Errors were calculated directly from the counting statistics.

Accumulation rates were calculated by applying a constant flux model to profiles of excess Pb-210 activity with depth in the seabed (Oldfield and Applyby 1984). If deep sediment mixing (i.e., below the surface mixed layer) occurred in the deposit, the calculated accumulation rate is a maximum estimate of the actual accumulation rate. Calculated Pb-210 accumulation rates are termed "apparent accumulation rates" until verified using a complementary tracer (Cs-137, see below).

Cs-137 (half-life 30.0 yr) is a particle-reactive, impulse tracer (produced from atmospheric nuclear tests), which was first introduced into the environment in significant amounts in 1954. In non-bioturbated sediments, two activity peaks are commonly preserved in Cs-137 profiles, a minor peak corresponding to 1959 (because of a moratorium on atmospheric tesing from 1958–1961) and a major peak representing the acme of atmospheric weapons testing in 1963–1964. These peaks provide an independent estimate of the sediment accumulation rate.

The Cs-137 activity on particles can be used to indicate whether the sediment is derived primarily from freshwater or marine sources (Mulholland and Olsen 1992). Particles derived from freshwater environments are enriched in Cs-137 relative to
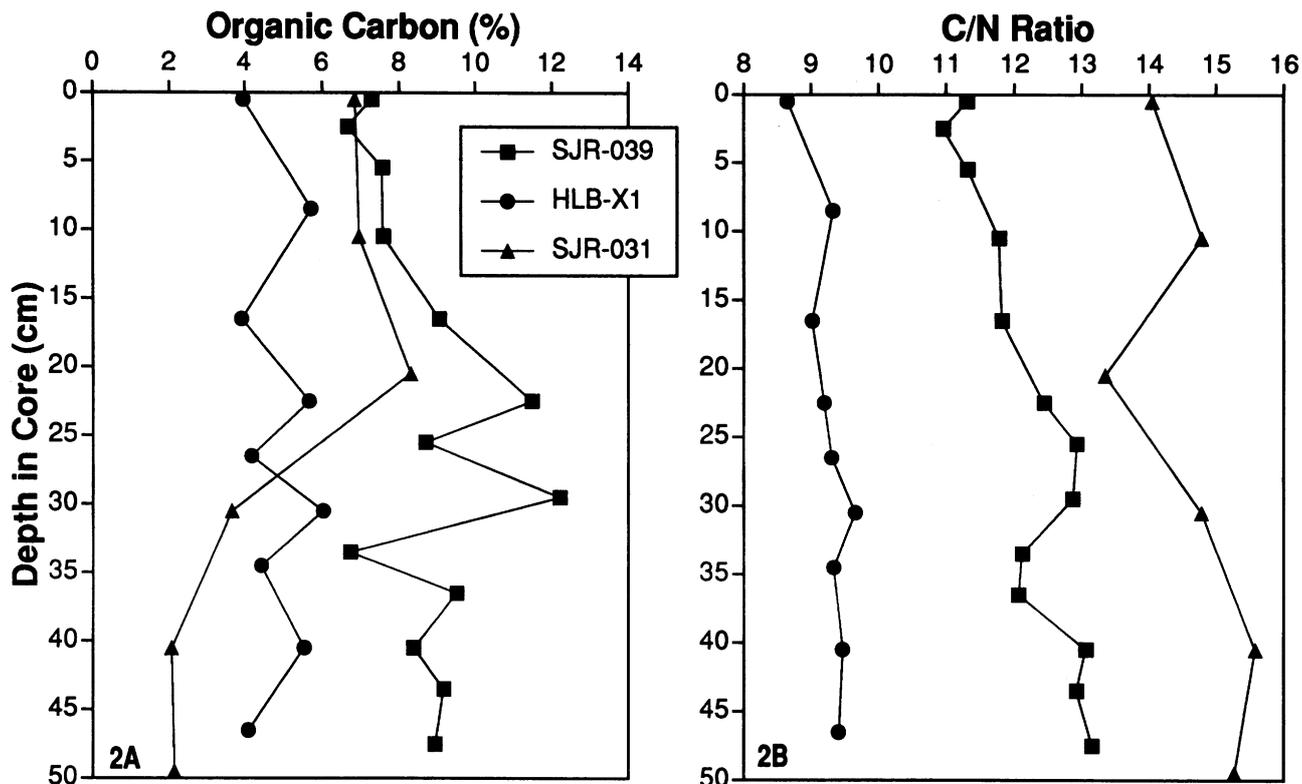
Fig. 2.   Comparison of geochemical properties in SJR-039, SJR-031, and HLB-X1. A) Organic carbon content. B) Carbon to nitrogen ratio. Note the distinct difference between cores SJR-039 and SJR-031, separated by only 4.5 km, resulting from differences in vegetation.

particles derived from marine environments. In fresh water, Cs-137 is rapidly adsorbed onto particle surfaces and migrates over a period of weeks to years into clay interlayer sites (Evans et al. 1983; Comans et al. 1991). Cs-137 in the interlayer sites is relatively nonexchangeable whereas the surficial adsorbed fraction can be desorbed upon introduction of the particles into saline waters (Zucker et al. 1984). Laboratory studies show that this exchangeable fraction is less than 15% of the Cs-137 activity on freshwater particles (Robertson et al. 1973; Olsen et al. 1989). In saline environments Cs activity on particles is generally low because of competition between Cs and other cations (especially K^+) for adsorption sites (Mulholland and Olsen 1992).

Results and Discussion

St. Johns River

Elemental Geochemistry

The trace-metal concentrations for the St. Johns River cores are presented in Table 1. In SJR-039, aluminum concentration varies from 3.7% to 7.3% but does not exhibit any significant trend. Organic carbon ranges between 6.6% and 12.2% (Fig. 2A)

and calcium carbonate decreases from 15% to 9% downcore. In contrast, aluminum decreases downcore from 5.8% to 1.8% in SJR-031. This decrease in aluminum is accompanied by a decrease in calcium carbonate (from 18.9% to 3.5%) and organic carbon (from 6.8% to 2.1%; Fig. 2A), suggesting that quartzose materials comprise a greater proportion of the sediment downcore. However, field observations of grain size indicate that quartz sand becomes significant only in the lower 10 cm of the core. Although variation in the carbon content is present, the source of carbon has been relatively constant over time based on profiles of the C:N ratio; the monotonic increase of the ratio is common and results from preferential remineralization of nitrogen (Fig. 2B). The sizable variation in organic carbon content downcore is not obviously reflected by changes in the C:N ratio. The relatively high sediment C:N ratio in SJR-031 probably reflects the dominance of *Juncus roemerianus* (black needlerush) along the river in its lower reaches (DeMort 1991).

Geochronology

The apparent Pb-210 accumulation rate for SJR-039 is 1.1 cm yr^{-1}, suggesting that this core pro-

TABLE 1.   Metal concentrations in cores from estuarine environments in Florida. Each value represents the average of duplicate analyses.

Core	Depth	Al (%)	As (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Pb (ppm)	Ni (ppm)	Zn (ppm)
SJR-039	0–1	5.07 ± 0.12	8.11 ± 0.09	1.20 ± 0.01	82.8 ± 0.4	36.8 ± 0.5	58.9 ± 1.3	18.8 ± 0.2	160 ± 3.0
	2–3	6.92 ± 0.07	10.50 ± 0.34	1.28 ± 0.29	90.1 ± 2.3	39.9 ± 2.5	74.5 ± 8.6	20.9 ± 1.7	170 ± 15.0
	5–6	7.28 ± 0.13	8.54 ± 0.93	1.36 ± 0.10	98.6 ± 1.1	43.3 ± 1.1	75.8 ± 0.3	23.3 ± 0.9	197 ± 7.0
	10–11	6.94 ± 0.09	7.80 ± 1.20	1.30 ± 0.08	94.9 ± 3.7	43.7 ± 1.9	83.3 ± 0.7	22.6 ± 1.0	196 ± 5.0
	16–17	5.79 ± 0.02	6.82 ± 0.45	1.34 ± 0.12	82.5 ± 1.1	29.1 ± 0.2	65.6 ± 6.0	19.8 ± 0.5	138 ± 1.0
	22–23	5.91 ± 0.17	6.77 ± 0.94	2.85 ± 0.06	90.7 ± 2.6	22.6 ± 0.6	44.8 ± 2.1	18.4 ± 0.8	104 ± 2.0
	25–26	4.20 ± 0.35	5.45 ± 0.32	2.20 ± 0.21	81.6 ± 1.4	23.6 ± 1.6	50.1 ± 3.3	16.3 ± 0.5	106 ± 7.0
	29–30	4.19 ± 0.51	7.06 ± 0.23	1.91 ± 0.08	55.0 ± 4.6	21.7 ± 1.3	40.2 ± 1.9	16.3 ± 0.7	96.9 ± 3.3
	33–34	3.74 ± 0.30	4.18 ± 0.38	1.72 ± 0.12	54.7 ± 2.4	13.3 ± 0.3	22.1 ± 1.3	10.7 ± 1.4	56.9 ± 0.4
	36–37	5.11 ± 0.34	7.29 ± 0.02	2.35 ± 0.01	56.0 ± 1.2	18.1 ± 0.1	25.3 ± 3.8	16.6 ± 0.1	79.6 ± 0.2
	40–41	5.62 ± 0.10	5.41 ± 2.74	1.73 ± 0.04	69.4 ± 0.1	13.9 ± 0.3	27.7 ± 1.1	12.3 ± 1.1	66.4 ± 0.5
	43–44	5.14 ± 0.15	9.36 ± 0.18	1.89 ± 0.09	58.5 ± 5.3	18.6 ± 0.1	30.6 ± 0.1	18.1 ± 1.6	90.8 ± 3.3
	47–48	4.92 ± 0.14	9.08 ± 0.39	2.19 ± 0.03	96.5 ± 5.8	21.4 ± 1.7	43.1 ± 0.8	18.6 ± 0.4	109 ± 7.0
SJR-031	0–1	3.93 ± 0.17	7.05 ± 0.66	1.06 ± 0.06	48.7 ± 2.7	24.9 ± 0.1	34.4 ± 8.7	15.1 ± 0.1	100 ± 3.0
	10–11	4.30 ± 0.96	6.28 ± 0.49	1.28 ± 0.01	50.8 ± 0.1	24.8 ± 5.0	34.5 ± 3.6	15.1 ± 0.2	88.6 ± 1.2
	20–21	5.83 ± 0.11	7.97 ± 0.40	0.75 ± 0.04	54.8 ± 4.2	14.6 ± 0.1	26.0 ± 1.7	15.8 ± 0.1	63.8 ± 0.7
	30–31	3.46 ± 0.13	3.35 ± 0.88	0.45 ± 0.01	34.5 ± 3.7	10.3 ± 0.7	16.7 ± 1.4	8.1 ± 0.6	43.9 ± 1.9
	40–41	1.78 ± 0.36	3.16 ± 1.00	0.20 ± 0.04	20.7 ± 5.6	3.1 ± 0.7	4.8 ± 0.4	4.3 ± 0.2	12.0 ± 0.7
	49–50	2.78 ± 0.12	2.77 ± 0.11	0.23 ± 0.01	30.4 ± 2.7	5.1 ± 0.3	6.9 ± 0.3	6.1 ± 0.7	18.1 ± 0.7
HLB-X1	0–1	6.82 ± 0.14	7.60 ± 1.69	2.61 ± 0.36	156 ± 7.0	54.5 ± 3.0	119 ± 1.7	26.6 ± 1.1	223 ± 8.0
	8–9	5.67 ± 0.12	4.30 ± 1.10	2.72 ± 0.00	102 ± 6.5	53.8 ± 2.2	121 ± 1.8	23.3 ± 0.9	177 ± 0.0
	16–17	7.14 ± 0.42	7.29 ± 0.98	3.28 ± 0.11	185 ± 1.3	60.8 ± 0.5	167 ± 3.1	32.5 ± 1.2	267 ± 1.0
	22–23	4.98 ± 0.13	4.94 ± 0.67	2.42 ± 0.16	95.0 ± 0.6	45.6 ± 1.0	165 ± 9.5	22.6 ± 0.4	165 ± 8.0
	26–27	6.79 ± 0.07	5.33 ± 1.13	3.03 ± 0.01	186 ± 7.9	60.4 ± 1.8	197 ± 0.7	31.7 ± 1.1	262 ± 10.0
	30–31	4.73 ± 0.14	4.97 ± 0.80	2.09 ± 0.11	90.0 ± 4.2	37.8 ± 3.5	148 ± 10.2	20.7 ± 2.0	130 ± 9.0
	34–35	7.01 ± 0.07	7.98 ± 0.60	3.29 ± 0.05	192 ± 3.1	56.4 ± 1.3	210 ± 1.6	33.3 ± 2.7	251 ± 7.0
	40–41	4.06 ± 0.14	5.31 ± 0.81	1.97 ± 0.0	85.0 ± 1.0	39.9 ± 0.7	156 ± 9.5	22.4 ± 1.2	136 ± 3.0
	46–47	7.00 ± 0.03	6.92 ± 2.25	2.82 ± 0.20	195 ± 12.8	61.5 ± 0.6	185 ± 2.9	35.2 ± 1.0	233 ± 3.0

St. Johns River 039
S = 1.1 cm/y

Pb-210 Activity (dpm/g)

St. Johns River 031
S = 0.1 cm/y

Pb-210 Activity (dpm/g)

Hillsborough Bay - X1
S = 1.0 cm/y

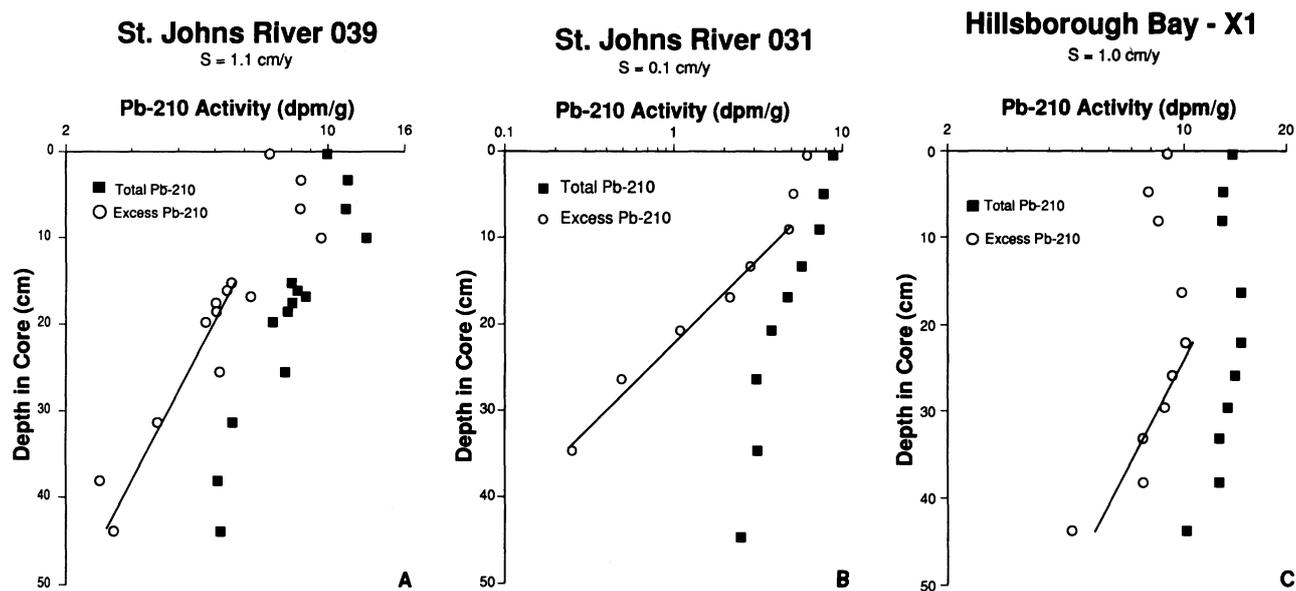### Pb-210 Activity (dpm/g)

Fig. 3. Plots of Pb-210 activity with depth in the sediment used to determine rates of sediment accumulation in this study. A) SJR-039. High rate (1.1 cm yr^{-1}) suggests that this core represents ~50 yr of accumulation. B) SJR-031. Low rate (0.1 cm yr^{-1}) indicates that this core contains a longer record of metal contamination. C) HLB-X1. High rate (1.0 cm yr^{-1}) indicates that this core also represents ~50 yr of accumulation.

vides a record of metal accumulation spanning approximately 50 yr (Fig. 3A). The supported levels of Pb-210 in the core are relatively constant at 2.0–2.5 dpm g^{-1} with depth. The X-radiograph of this core diplays a well-laminated, muddy sediment, with what appear to be synaeresis cracks in the upper 11 cm and scattered gas voids below. Given this calculated accumulation rate, the 1963–1964 Cs-137 peak should lie at 26 cm. The peak is observed in the 23–24 cm interval (Fig. 4). An accumulation rate calculated from the location of this peak would be 0.9 cm yr^{-1}. Modeling of the Cs-137 penetration depth (DeMaster et al. 1985) demonstrates that the calculated accumulation rate is within 3% of the actual rate, and is not significantly affected by sediment mixing. The good agreement between the rate calculated from the Cs-137 profile and the calculated Pb-210 rate indicates that the apparent rate is a good estimate of the actual accumulation rate.

The two-component mixing model used by Mulholland and Olsen (1992) can be used to provide a first-order approximation of the relative contribution from riverine and oceanic sources to the area represented by SJR-039. Mulholland and Olsen (1992) measure a riverine end-member Cs-137 activity for bottom sediments of 3.0 dpm g^{-1} in the Savannah River. The oceanic end-member along the northeastern Florida coast is approximately 0.02 dpm g^{-1} (Alexander unpublished data),

in agreement with Mulholland and Olsen's value of 0.012 dpm g^{-1}. Using these values and a surface activity of 2.41 dpm g^{-1}, the maximum amount of sediment derived from oceanic sources is approximately 20% in SJR-039. This is a maximum estimate because the Cs-137 riverine end-member in Mulholland and Olsen's study area is elevated as a result of Cs discharges from the United States Department of Energy's Savannah River Site. Any decrease in the riverine end-member activity would decrease further the fraction of marine particles in the core. The relatively high Cs-137 specific activities in SJR-039 in the presence of saline overlying waters further supports the riverine origin, indicating that these sediments equilibrated with Cs-137 in a freshwater environment (Mulholland and Olsen 1992).

The apparent accumulation rate of SJR-031, 0.1 cm yr^{-1}, is an order of magnitude lower than that of SJR-039 (Fig. 3B). The X-radiograph of this core reveals that the upper 10 cm is bioturbated, and the lower portion is laminated. The upper, bioturbated layer roughly represents the past 100 yr of metal accumulation (from the apparent accumulation rate), thereby reducing the usefulness of this core for recent historical records of contamination. However, the longer geologic record contained in the lower, laminated portion of this core provides verification for data from SJR-039. Bioturbation of the upper 10 cm and low specific Cs-

137 activities in this core preclude the vertification of the apparent Pb-210 rate with Cs-137 data (Fig. 4). The low activities probably indicate a more oceanic source for the sediments in this core. The two component mixing model (Mulholland and Olsen 1992) predicts that approximately 90% of the particles in SJR-031 have a marine origin. Core SJR-031 was collected approximately 4.5 km seaward of SJR-039, suggesting that the region between them (i.e., the narrow, restricted bend in the river through downtown Jacksonville; Fig. 1A) represents a boundary between landward transport of marine particles and seaward transport of riverine material. SJR-039 represents an area where the river widens significantly and that may be a depocenter for riverine sediment. The low accumulation rate in the area represented by SJR-031 may result primarily from a decrease in riverine sediment supply.

Enrichment Factors

Enrichment factors for SJR-039 and SJR-031 are shown in Table 2 and are referenced to the upper 95% confidence interval of the metal vs. aluminum plots in the uncontaminated sediment database developed by Windom et al. (1989) and Schropp et al. (1990). The present study compares measured metal concentrations to this higher threshold for uncontaminated sediment values for greater statistical significance in our estimates of enrichment. Enrichment factors referenced to the linear regression line through the data (i.e., average value) are shown in parentheses for comparison with other published data. If the average line is used to determine enrichment factors, all metals (with the exception of As) are enriched in both cores from the St. Johns River. Arsenic exhibits depletion in all samples analyzed in this study. The geochemistry of arsenic is not as well constrained in coastal and estuarine environments as is that of other metals (see, for example, Howard et al. 1984; Sanders 1985; Byrd 1988, 1990).

Sediments in SJR-039 are enriched in Cd, Pb, and Zn and display a general trend of increasing enrichment with time (Fig. 5A). Table 2 presents the calculated enrichment factors. Cadmium is the most enriched of the metals studied, with an enrichment factor of 2.1–3.4 prior to about 1970. Between 1970 and 1975, the enrichment factor decreased dramatically to ~1.5, where it remains. The enrichment factor in SJR-031 at the surface is very similar to that of SJR-039 (1.42 vs. 1.50) and only decreases below enriched levels between 100 y.b.p. and 200 y.b.p. (Fig. 5B). Jacksonville was the major port city on Florida's east coast by the 1840s, and enriched cadmium concentrations
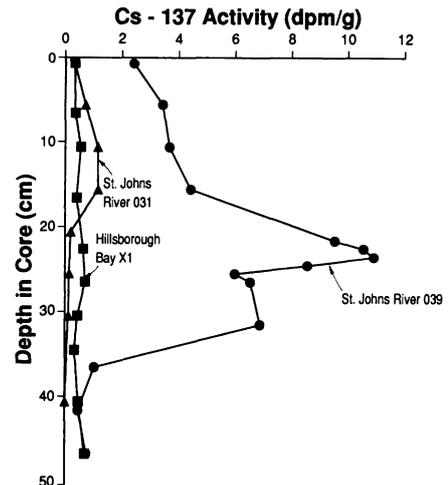

Fig. 4. Comparison of Cs-137 activity with depth. High specific activity on particles in SJR-039 indicate that sediment in this core is derived primarily from freshwater sources. Low activities in SJR-031 and HLB-X1 indicate that these sites are dominated by marine sources.

could have been present as early as this time (Anderson unpublished data). Although the time of decrease to background levels in SJR-031 is not tightly constrained, it provides a first estimate of the timing of the cadmium contamination.

Several events occurred during the early to mid 1970s that could help explain the variation in cadmium. Cadmium geochemistry is strongly influenced by biogeochemical nutrient cycling (Collier and Edmond 1984). There is a marked decrease in carbon content in the upper portion of SJR-039, beginning at approximately the same horizon as the decrease in cadmium enrichment, suggesting that a decrease in carbon flux may have occurred at the same time. One significant source of carbon to the St. Johns River within this time frame was water hyacinth. Water hyacinth, an introduced aquatic plant, effectively choked the St. Johns River prior to 1974–1975 (J. Joyce, Center for Aquatic Plants, University of Florida, personal communication). At that time, an effective, aggressive management program was carried out to significantly reduce the plants. Prior to 1974–1975, the plants were a significant source of organic carbon to the river (5 tons organic matter acre^{-1} yr^{-1}; J. Joyce, Center for Aquatic Plants, University of Florida, unpublished data).Water hyacinth are known to sequester metals within their tissues, stripping cadmium from the water column, and delivering it to the river bed (Joyce 1985; Blake et al. 1987; Nir et al. 1990). This observation suggests that dissolved cadmium levels should have increased significantly in conjunction with the de-

TABLE 2. Metal enrichment factors in cores from estuarine environments in Florida. Values referenced to the upper 95% confidence interval for regional sediment database, values in parentheses referenced to linear regression (see text for discussion).

| Core	Depth	As	Cd	Cr	Cu	Pb	Ni	Zn
SJR-039	0–1	0.08 (0.56)	1.50 (8.22)	0.60 (3.00)	0.83 (3.22)	1.22 (2.72)	0.72 (2.98)	1.33 (4.61)
	2–3	0.09 (0.59)	1.46 (8.01)	0.55 (2.76)	0.77 (3.01)	1.23 (2.75)	0.72 (2.98)	1.13 (3.93)
	5–6	0.07 (0.47)	1.53 (8.39)	0.59 (2.94)	0.82 (3.18)	1.20 (2.69)	0.78 (3.27)	1.27 (4.39)
	10–11	0.08 (0.49)	1.48 (8.13)	0.58 (2.90)	0.85 (3.29)	1.37 (3.07)	0.77 (3.22)	1.30 (4.52)
	16–17	0.07 (0.43)	1.61 (8.83)	0.56 (2.78)	0.61 (2.39)	1.23 (2.76)	0.72 (3.00)	1.04 (3.62)
	22–23	0.06 (0.42)	3.40 (18.67)	0.60 (3.03)	0.47 (1.84)	0.83 (1.85)	0.67 (2.77)	0.78 (2.69)
	25–26	0.06 (0.42)	2.90 (15.91)	0.65 (3.28)	0.58 (2.56)	1.19 (2.66)	0.66 (2.76)	1.01 (3.49)
	33–34	0.05 (0.35)	2.34 (12.87)	0.47 (2.34)	0.35 (1.35)	0.57 (1.28)	0.45 (1.88)	0.59 (2.04)
	40–41	0.05 (0.35)	2.10 (11.50)	0.48 (2.38)	0.30 (1.16)	0.53 (1.19)	0.45 (1.88)	0.51 (1.78)
	47–48	0.10 (0.63)	2.75 (15.13)	0.71 (3.55)	0.49 (1.90)	0.91 (2.04)	0.72 (2.98)	0.93 (3.21)
SJR-031	0–1	0.09 (0.57)	1.42 (7.81)	0.40 (2.03)	0.63 (2.46)	0.86 (1.92)	0.63 (2.61)	1.00 (3.45)
	10–11	0.07 (0.48)	1.67 (9.20)	0.40 (2.01)	0.60 (2.34)	0.81 (1.80)	0.61 (2.53)	0.83 (2.87)
	20–21	0.08 (0.50)	0.90 (4.93)	0.37 (1.84)	0.31 (1.19)	0.49 (1.09)	0.57 (2.39)	0.48 (1.66)
	30–31	0.04 (0.29)	0.63 (3.44)	0.31 (1.54)	0.30 (1.08)	0.46 (1.02)	0.35 (1.46)	0.48 (1.66)
	40–41	0.06 (0.42)	0.34 (1.86)	0.26 (1.32)	0.12 (0.45)	0.21 (0.48)	0.23 (0.97)	0.21 (0.73)
	49–50	0.04 (0.28)	0.34 (1.87)	0.30 (1.52)	0.15 (0.60)	0.22 (0.50)	0.29 (1.19)	0.23 (0.80)
HLB-X1	0–1	0.07 (0.43)	2.98 (16.40)	0.96 (4.82)	1.06 (4.13)	1.98 (4.43)	0.92 (3.81)	1.50 (5.20)
	8–9	0.04 (0.28)	3.28 (18.03)	0.70 (3.48)	1.15 (4.46)	2.30 (5.16)	0.85 (3.56)	1.36 (4.71)
	16–17	0.06 (0.40)	3.70 (20.34)	1.11 (5.57)	1.16 (4.51)	2.69 (6.02)	1.10 (4.59)	1.74 (6.03)
	22–23	0.05 (0.34)	3.03 (16.66)	0.69 (3.48)	1.03 (4.02)	3.45 (7.71)	0.87 (3.61)	1.39 (4.81)
	26–27	0.05 (0.34)	3.47 (19.06)	1.15 (5.76)	1.18 (4.59)	3.29 (7.36)	1.09 (4.55)	1.77 (6.13)
	30–31	0.05 (0.36)	2.66 (14.60)	0.68 (3.40)	0.88 (3.42)	3.21 (7.20)	0.81 (3.36)	1.13 (3.93)
	34–35	0.07 (0.45)	3.73 (20.51)	1.17 (5.84)	1.09 (4.22)	3.43 (7.67)	1.14 (4.73)	1.66 (5.79)
	40–41	0.06 (0.42)	2.62 (14.39)	0.69 (3.47)	1.00 (3.88)	3.78 (8.46)	0.92 (3.83)	1.32 (4.58)
	46–47	0.06 (0.39)	3.20 (17.59)	1.19 (5.94)	1.18 (4.61)	3.02 (6.77)	1.20 (5.00)	1.54 (5.34)
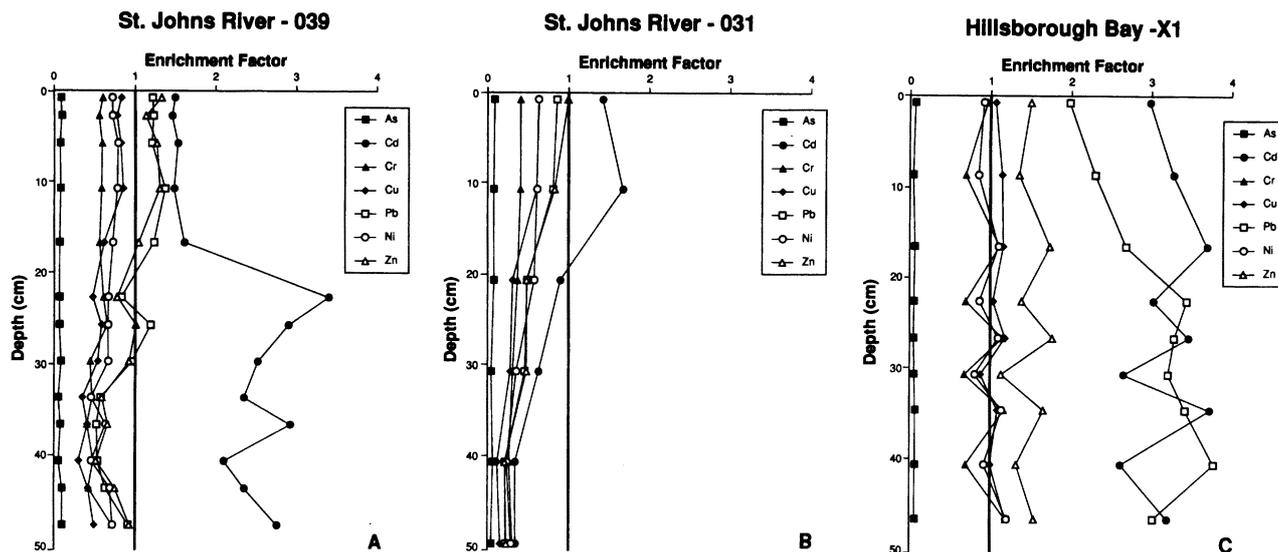
Fig. 5.   Plots of historical trends in metal enrichment factors. A) SJR-039. Note the dramatic decrease in Cd enrichment, and the trend of increasing enrichment of the other metals. B) SJR-031. The general trend is one of increasing enrichment with time. C) HLB-X1. Note the generally metal-enriched nature of this core, the lack of significant trends for most of the metals, and the significant decrease in Pb and Cd.

crease in hyacinth uptake and in sediment concentration. Other significant events that may have influenced the decrease in cadmium levels include the peak in 1968 of pollutant discharge to the river and elimination of the last raw sewage outfall in 1977 (Anderson unpublished data). In addition, elevated cadmium levels are associated with gypsum and phosphate processing, and these industries may have contributed significantly to the riverine burden of cadmium prior to effluent regulation. Most of these industries were connected to the regional sewer system or built their own treatment plants during the early 1970s (Anderson unpublished data).

Enrichment factors are also >1 for Pb and Zn in SJR-039 (Fig. 5A). These two metals are good proxies for nonlocalized input pollutants, and exhibit increasing enrichment with time. These metals reached a maximum in enrichment sometime between 1975 and 1981, and have been relatively constant at a slightly reduced level since that time. Of the two metals, the slight decrease in sediment Pb levels is more convincing, and is most probably a result of the decrease in leaded gasoline use. Sediments are still enriched by a factor of 1.22, however.

SJR-031 sediments are not enriched in any metal but cadmium (Fig. 5B). However, the trend in all the metals (with the exception of As) is one of increasing enrichment with time. Enrichment factors are low (0.1–0.3) for metals in the bottom of the core. At the sediment surface, enrichment factors have increased to 0.4–1.0 (excluding Cd at 1.42), indicating a progressive increase in anthropogenic loading to the system.

HILLSBOROUGH BAY

Elemental Geochemistry

Metal concentrations in Hillsborough Bay (core HLB-X1) are presented in Table 1. Geochemical properties seem to exhibit a repetitive alternation with depth in this core. Aluminum concentration (4.7–7.1%) alternates repetitively downcore (on scales of 4–8 cm) and is inversely correlated with repetitive variation in organic carbon content (3.9–6.0%; Fig. 2A). This scale of repetition is also observed in the X-radiograph, which exhibits laminae 4–7 cm thick. Metal concentration covaries with aluminum concentration (compare aluminum data in Table 1 and Fig. 5C). The surficial calcium carbonate concentration (33.3%) is higher than values in the rest of the core. Calcium carbonate exhibits a slight increase from ~22% to ~28% (average 25.6 ± 2.5%) downcore from the first subsurface interval, but does not exhibit repetitive downcore variations. Calcium carbonate is likely to be produced in situ, whereas aluminum represents allochthonous material. Thus the repetitious nature of the sediment properties probably represents variation in the character of sediment discharged to Hillsborough Bay. Alternatively, these particles may be older sediment resuspended by harbor maintenance dredging (Lewis and Estevez

1988). Field observations of grain size in HLB-X1 indicate that sediments are fine-grained silt and clay throughout the core.

The C:N ratio increases with depth in the upper 8 cm (from 8.65 to 9.33), and is essentially constant below this depth (9.34 ± 0.19; Fig. 2B). In contrast to the St. Johns River, C:N ratios in Hillsborough Bay are much closer to those expected for labile organic matter. Frequent and prolonged phytoplankton blooms are common in Hillsborough Bay (Lewis and Estevez 1988), and represent a source for labile organic matter to the seabed. Doyle et al. (1989) suggest that a decrease in the C:N ratio at the sediment-water interface between the surveys in 1963 and 1986 represents an increase in organic nitrogen deposition in the bay that is not accompanied by a commensurate increase in organic carbon flux. Our C:N data, coupled with the geochronology for HLB-X1 (see below), indicate that this increase in nitrogen flux, if real, has occurred predominantly since 1981.

Geochronology

The apparent Pb-210 accumulation rate for HLB-X1 is 1.0 cm yr^{-1} (Fig. 3C). Cs-137 activity is uniformly low throughout the core, and thus the profile cannot be used to verify the calculated Pb-210 accumulation rate (Fig. 4). The levels of Pb-210 are relatively constant downcore (4.32–5.74 dpm g^{-1}), but are over twice those observed in many other areas, including the St. Johns River (see, for example, DeMaster et al. 1985; Kuehl et al. 1986; Alexander et al. 1991). Tampa Bay waters are enriched in Rn-222, a daughter product of Ra-226, and thus presumably in Ra-226 as well (Fanning et al. 1982; Doyle et al. 1989). Relatively high levels of radioactivity from uranium and its daughter products in the phosphate-rich Hawthorn Formation underlying Hillsborough Bay and from phosphate processing facilities located near the bay may contribute to these elevated Rn-222 levels. This enrichment may result in higher sediment activities because we calculate Ra-226 activity by measuring the activity of the Ra-226 granddaughters Pb-214 and Bi-214 (that result from the decay of Rn-222).

Enrichment Factors

Enrichment factors for HLB-X1 are shown in Table 2 and Fig. 5C. This core demonstrates the utility of normalization to aluminum and of a regional uncontaminated database. Although some of the variability observed in geochemical properties downcore is present in the enrichment factor profile (Fig. 5C), contaminated sediments are clearly delineated from those that are not. Referenced to uncontaminated sediments from the region, it is not critical to reach "background" levels in cores. Indeed, in areas where sediment accumulation is rapid, retrieving sediment representing pre-industrial metal levels may be difficult or impossible.

As in the St. Johns River, Cd, Pb, and Zn are enriched in Hillsborough Bay sediments. Cd and Pb values in the bay are similar to those in San Francisco Bay (Long et al. 1991). The other metals analyzed in this study (Cr, Cu, Ni) border on enrichment, with the exception of As. A trend of declining Pb enrichment begins between 1969 and 1974, and continues to the present, as expected from the decrease in leaded gasoline usage. Cd exhibits a trend similar to that of Pb, with similar timing. The Zn enrichment is relatively constant downcore. Pb and Zn covaried in the St. Johns River, suggesting well-mixed, nonlocalized input for these metals in that area. The dissimilar enrichment trends for Pb and Zn in Hillsborough Bay indicate that there is probably an additional source of Pb. High Pb levels (200–800 ppm dry weight) in cores from the lower Hillsborough River indicate that this river is probably an important source of Pb to the bay (Trefry et al. 1989).

REGIONAL INTEGRATION

Historical profiles of metal accumulation generated for the lower St. Johns River and Hillsborough Bay, Florida, demonstrate that Cd, Pb, and Zn are enriched in these estuarine areas. These results can be generalized to the whole Florida coastal zone by comparing our results to a recently published, comprehensive Florida sediment atlas (Seal et al. 1993). This atlas shows that enrichment factors are greater than 1 for Pb, Cd, and Zn in virtually all urban Florida coastal areas. These urban areas represent about 35% of the area covered by the atlas (1,500 samples). These data and the results of our study suggest that metal enrichment is significant in much of the Florida coastal zone, and will probably increase as urbanization encroaches upon undeveloped areas.

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