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Historical Trace Element Distribution in Sediments from the Mississippi River Delta

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ABSTRACT: Five sediment cores were collected on the shelf of the inner Mississippi Bight in June 2003 for a suite of radionuclides to establish geochronologies and trace elements to examine patterns of contaminant deposition and accumulation. Core sites were chosen to reflect a matrix of variable water depths, proximity to the Mississippi River mouth as the primary source for terrigenous particles, and extent and duration of summertime water column hypoxia. The vertical distribution of ^{239,240}Pu and ^{210}Pb$_{xs}$ ($= {}^{210}$Pb$_{total} - {}^{226}$Ra) provided reliable geochronological age constraints to develop models for mass accumulation rates and historic trace element inputs and variations. Mass accumulation rates ranged from 0.27 to 0.87 g cm^{-2} yr^{-1} and were internally consistent using either ^{210}Pb$_{xs}$ or ^{239,240}Pu. Measured inventories of ^{137}Cs, ^{239,240}Pu, and ^{210}Pb$_{xs}$ were compared to atmospheric deposition rates to quantify potential sediment focusing or winnowing. Observed variability in calculated mass accumulation rates may be attributed foremost to site-specific proximity to the river mouth (i.e., sediment source), variability in water depth, and enhanced sediment focusing at the Mississippi River canyon site. Trace element concentrations were first normalized to Al, and then Al-normalized enrichment factors (ANEF) were calculated based on preanthropogenic and crustal trace element abundances. These ANEFs were typically > 1 for V and Ba, while for most other elements studied, either no enrichment or depletion was observed. The enrichment of Ba may be related, in part, to the seasonal occurrence of oxygen-depleted subsurface waters off the Mississippi River delta, as well as being an ubiquitous by-product of the petroleum industry.

Introduction

Fine-grained sediments accumulating off large river mouths can provide a useful record to reconstruct historic off-continent material flux estimates (Nittrouer et al. 1984; Trefry et al. 1986; Van Metre et al. 1998; Wheatcroft and Sommerfield 2005). The vertical distribution of contaminants in dated sediment cores has been used in this manner to obtain information on the extent and history of trace element input and postdepositional alteration (e.g., Goldberg et al. 1979; Valette-Silver 1993; Connor and Thomas 2003; Monterroso et al. 2003; Turner et al. 2004). Many contaminants carried downstream by rivers and exposed to turbid coastal waters have a strong affinity for reactive surface sites of fine-grained suspended particulate matter (Benoit et al. 1994; McKee et al. 2004). During estuarine transport, such fine-grained particulate matter may undergo coagulation or aggregation and settle out of the water column and be deposited on the seabed for eventual longer-term accumulation. Information on past trace element levels derived from such sedimentary records can be useful to improve coastal management strategies,

as well as to assess the success of pollution control measures. Particle-bound trace elements can be released or mobilized as a result of both natural processes and human-induced activities, and may become readily enriched in coastal waters and sediments (Windom et al. 1989; Swarzenski et al. 1995). It is well documented that the first substantial pulse of metals and trace elements introduced into the environment started in the early 1800s and peaked between the 1940s and 1970s (Cloern 2001). After the implementation of the Clean Air Act and other regulatory measures in North America and Europe, pollutant levels in coastal and estuarine systems began to decline after the late 1970s, indicating that mitigating measures have often been effective and successful (Valette-Silver 1993; Cloern 2001).

The focus of this study lies in reconstructing historic contaminant inputs and inventories within a 100-yr window. Quantitative interpretation of observed trace element concentrations and inventories requires a precise site-specific sediment geochronology. In estuarine and coastal environments, postdepositional mixing of sediments by physicochemical and biological mechanisms may alter the original contaminant imprint on the sediments (Aller and Cochran 1976; Crusius et al. 2004). Physical sediment mixing processes in the Missis-

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sippi Bight may include slump-collapse features, subsidence, bathymetry-based sediment focusing, and storm-related effects.

The down core variation in $^{210}Pb_{xs}$ ($= ^{210}Pb_{total} - {}^{226}Ra$) activities in coastal sediments has been extensively used (e.g., Nittrouer et al. 1984) to determine linear sedimentation rates (cm yr^{-1}) or mass accumulation rates (g cm^{-2} yr^{-1}). The combined application of $^{239,240}Pu$ and $^{210}Pb_{xs}$ has been developed specifically to delineate mixing processes from sedimentation (e.g., Benninger et al. 1979; Santschi et al. 1984; Ravichandran et al. 1995). Pu isotopes are an excellent analog for studies of heavy metal transport through the environment, because Pu is highly particle reactive and has a well-defined input function (Santschi et al. 1980, 1984).

The Mississippi River remains the single largest source of fresh water and sediment to the Gulf of Mexico (Meade and Parker 1985). Major contaminant inputs to the Mississippi River include a wide range of industrial, municipal, and agricultural waste inputs (Meade 1995; Swarzenski and McKee 1998; Mitra et al. 2000; Mitra and Bianchi 2003). Contaminant distributions in fine-grained sediments in the coastal areas usually can be grouped into three categories (Bentley and Sheremet 2003; McKee et al. 2004): areas of little or no net deposition or accumulation of either sediment or sediment-hosted contaminants; areas where deposition is primarily a result of natural processes involving a balance of deposition, remobilization, and accumulation; and areas where deposition is physically accelerated (i.e., where sediment is focused).

We collected five sediment cores representing a matrix of variable water depths, distance from the river mouth, and degree of water column hypoxia, and measured the activities of $^{210}Pb_{xs}$, ^{226}Ra, $^{239,240}Pu$, and ^{137}Cs to establish site-specific geochronologies. A suite of solid-phase trace elements was also measured to assess the historic contaminant inputs and postdepositional variation within these sites. Because the trace elements observed in sediments have both a natural and anthropogenic signal, and the natural signal is highly dependent on grain size, mineralogy, and organic carbon content, the trace elements were normalized to Al (as a lithogenic reference element).

Materials and Methods

SAMPLING SITES

The Mississippi River basin drains about 2.9×10^6 km^2 or 40% of the conterminous United States. This river is directly or indirectly affected by a wide range of industry, agriculture, and municipalities (Meade 1995). It has been estimated that ca. 60% of
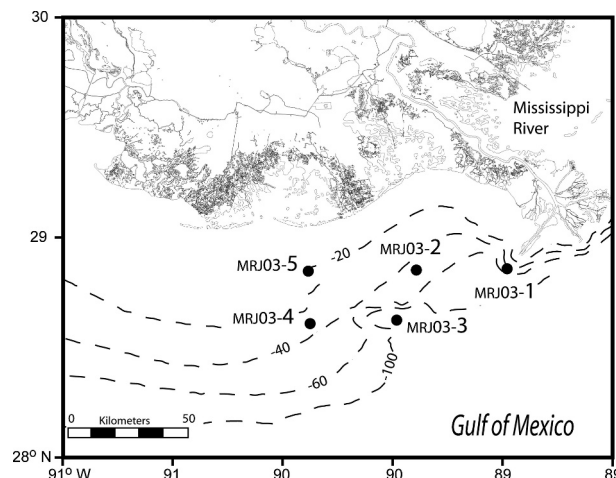

Fig. 1. Station location map of the five coring sites within the inner Mississippi Bight. Bathymetric contour lines depict 20-m intervals.

the dissolved material and 67% of the suspended solids from 48 states are transported by the Mississippi River (Curtis et al. 1973). Sediment cores were collected from a total of five sites in June 2003 in the inner Mississippi Bight (Fig. 1) onboard the R/V *Longhorn* using a large ($50 \times 50 \times 50$ cm) box corer, as well as a multicorer to carefully capture the sediment-water interface. Observations in water column dissolved oxygen (DO) content confirmed the presence of hypoxia (DO $<$ 2 mg l^{-1}) principally at core sites 5 and 2, where water depths were about 23 and 43 m, respectively (Table 1). There was no evidence of water column hypoxia at core sites 1 (22 m) and 3 (226 m). Upon the successful retrieval of a box core, a series of subcores were collected by pushing 3-inch diameter cylindrical plastic liners into the sediment, which were sectioned onboard into 1-cm intervals. Sediment from each depth interval was homogenized and transferred to either a precombusted glass jar (organics) or an acid-rinsed, preweighed plastic cup (inorganics and radionuclides), and stored frozen or chilled. Grain-size analyses were determined on a series of subcores using a Coulter LS 200 particle-size analyzer and approach 95% silt + clay in the bottom of cores 2, 3, 4, and 5.

The water content of each sediment interval was determined after drying at 90°C for 24 h. The porosity (ϕ) of each sample was calculated by assuming a solid density of 2.50 g cm^{-3} as follows:

$$\phi = f_w/[f_w + (1 - f_w)\rho_w/\rho_s] \qquad (1)$$

where f_w is the fraction of water in the wet sediment ($= 1 -$ dry weight/wet weight), ρ_w is the density of pore water (assumed to be 1.0 g cm^{-3}), and ρ_s is the density of dry sedimentary particles (assumed to be

TABLE 1.   Water depth, length, location, penetration depths (D, in cm), and inventories[1] of ^{137}Cs (I$_{Cs-137}$), ^{239,240}Pu (I$_{Pu-239,240}$), and excess ^{210}Pb (I$_{Pb-210xs}$; in dpm cm^{-2}) in five sediment cores collected from the inner Mississippi Bight (see Fig. 1 for site locations). Numbers in parenthesis denote the ratio of measured inventory to that of direct atmospheric input (i.e., retention efficiency); e.g., at core site 3 there is 386% more ^{239,240}Pu present than predicted from atmospheric fallout, indicating that sediment at this site is focused. NM = not measured.

Sample ID*	Core Length (cm)	Location	D$_{Pb-210xs}$	D$_{Cs-137}$	D$_{Pu-239,240}$	I$_{Cs-137}$	I$_{Pu-239,240}$	I$_{Pb-210xs}$
Core 1 (22.5 m)	50	28°52.546′N, 89°28.545′W	>50	>50	NM	10.7 ± 1.5 (2.96)	NM	110.9 ± 15.3 (3.39)
Core 2 (42.3 m)	50	28°53.427′N, 89°53.591′W	>50	35	>50	6.99 ± 1.07 (1.94)	0.69 ± 0.07 (2.46)	121.9 ± 8.0 (3.72)
Core 3 (226 m)	45	28°37.762′N, 90°00.620′W	>45	>45	>45	9.74 ± 0.99 (2.71)	1.08 ± 0.10 (3.86)	300.2 ± 14.3 (9.16)
Core 4 (32.2 m)	25	28°37.522′N, 90°22.647′W	>25	NM	NM	0.92 ± 0.69 (0.26)	NM	27.3 ± 10.0 (0.83)
Core 5 (22.9 m)	35	28°55.501′N, 90°22.501′W	35	>35	>35	1.22 ± 0.84 (0.34)	0.50 ± 0.04 (1.79)	30.1 ± 5.7 (0.92)

* Numbers in parenthesis denote total water depth.

2.5 g cm^{-3}). The cumulative mass depth (M) was calculated as:

$$M(mg\ cm^{-2}) = \sum [(1 - \phi_i)\rho_s \times \delta x] \quad (2)$$

where ϕ_i is the porosity at depth i and δx is the thickness of the layer (i.e., 1 cm). The dried core sections were pulverized using an agate mortar and pestle.

RADIOCHEMICAL AND TRACE ELEMENT ANALYSES

Two-gram aliquots of each of these powders were taken into solution by repeated digestion in concentrated HF, HNO$_3$, and HCl acid sequentially. A known amount of ^{209}Po spike was added at the beginning to assess the ^{210}Po recovery. Po was electroplated onto Ag planchets following the method of Flynn (1968) and assayed for ^{210}Pb (via ^{210}Po) by using an alpha spectrometer with a surface-barrier alpha detector coupled to InSpector (Canberra Industries Inc., Meriden, Connecticut). For ^{239,240}Pu, approximately 10 g of dried, powdered sample was leached with hot 6 M HCl three times. The leachates were combined and then processed for Pu after the addition of ^{242}Pu as a yield monitor (obtained from National Institute of Standards and Technology, NIST). The separation and purification of Pu were done by the standard ion-exchange technique (Baskaran et al. 1996). Approximately 10–15 g of dried, powdered sediment sample was placed in a gamma counting vial and specific concentrations of ^{226}Ra were determined using the 352 keV (^{214}Pb) and 609 keV (^{214}Bi) gamma lines for ^{226}Ra and the 661.6 keV line for ^{137}Cs. NIST radioactive spikes and material and International Atomic Energy Agency (IAEA) radioactive standards were used for calibrating the counting equipment. Precision in the activities of ^{210}Pb, ^{239,240}Pu, and ^{226}Ra was typically better than 5%. Since our radioactive

spikes are primary standards and our counting equipment was well calibrated, our accuracy was similar to our precision.

The inventories (I) of ^{210}Pb$_{xs}$, ^{137}Cs, and ^{239,240}Pu were calculated as follows:

$$I(dpm\ cm^{-2}) = A_n \times M \quad (3)$$

where M is the cumulative mass (=Σmass depth in each layer) corresponding to the depth interval (g cm^{-2}), and A$_n$ is the activity of the nuclide of interest (i.e., ^{210}Pb$_{xs}$, ^{137}Cs, or ^{239,240}Pu) per cumulative mass. The cumulative mass was calculated by combining the mass from each layer equivalent to the mass depth used for the determination of the radionuclides in each core. We believe that this is a better and simpler method of calculating the inventory of radionuclides as this one analysis will reduce the time and labor, as well as reduce the uncertainty in the extrapolation of activities from the measured layers to those unmeasured.

Dried and finely ground sediment samples were rigorously digested in concentrated HCl, HNO$_3$, HClO$_4$, and HF solutions and subsequently analyzed for a suite of trace elements using isotope dilution inductively coupled plasma mass spectrometry (ICP-MS). Reported detection limits (in μg g^{-1}) of the quadrupole ICP-MS for the select suite of trace elements are as follows: V (1), Mn (1), Pb (0.01), Cu (0.1), Li (0.5), Fe (100), Co (0.1), Cr (0.5), and Ba (0.5; Alexander et al. 1993). The analytical detection limit was less than 5% of the mean respective trace element concentrations. A series of triplicate analyses was run after every 15 samples, and these produced errors that were typically much less than 10%. Standard reference materials, blanks, spikes, and replicates were digested and analyzed prior to and after every sample set.
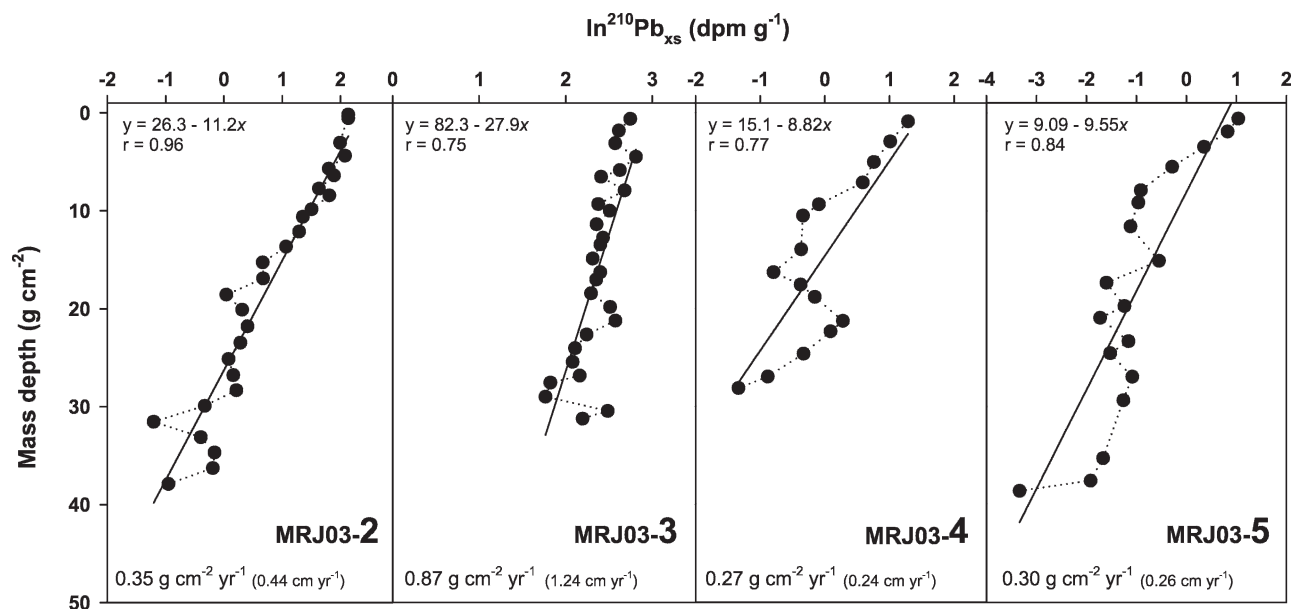
$\ln {}^{210}Pb_{xs}$ (dpm g^{-1})

Fig. 2. Vertical profiles of ln $^{210}Pb_{xs}$ activities (dpm g^{-1}) in sediments from cores 2, 3, 4, and 5.

Results and Discussion

GEOCHRONOLOGY

There are observed variations in the vertical distributions of $^{210}Pb_{xs}$ and $^{239,240}Pu$ activities in the five cores. Excess ^{210}Pb and $^{239,240}Pu$ penetration depths approach the full length of some of the cores (Table 1). The penetration depth of ^{137}Cs at core site 2 appeared to reach to a depth of 35 cm, whereas in other cores it was found to extend beyond the length of the core (data not shown). This can be attributed to the very low activities of ^{137}Cs, which are often at or below the limits of analytical detection.

At core site 1, $^{210}Pb_{xs}$ activities are very low, which suggests that there is no net accumulation of sediment at this site over the past several decades (plot not shown). Such scatter in $^{210}Pb_{xs}$ may be expected here since this site is located directly adjacent to the principal distributary of the Mississippi River (Southwest Pass) and is heavily influenced by active shipping and dredging. At other sites, $^{210}Pb_{xs}$ activities are found to decrease systematically down core and can be used to determine mass accumulation rates (Fig. 2). The penetration depths of $^{210}Pb_{xs}$ and $^{239,240}Pu$ in all the cores are close to or greater than the total core length retrieved.

A sediment geochronology may be developed by modeling the down core decrease of $^{210}Pb_{xs}$ and examining the vertical distribution of $^{239,240}Pu$ relative to the atmospheric fallout peak for Pu that occurred in 1963. $^{239,240}Pu$ is a by-product of atmospheric testing of nuclear weapons and was introduced into the environment around 1952 with a maximum fallout in 1963. In areas where the physical and biological mixing is negligible, the peak fallout retained in the sedimentary record corresponds to the year 1963. Any deviation from the expected atmospheric fallout in sediments is attributed to mixing, and the rates of mixing and sedimentation can be delineated or separated (Santschi et al. 1984; Ravichandran et al. 1995; Yeager et al. 2004).

A comparison of the linear sedimentation and mass accumulation rates using $^{210}Pb_{xs}$ and $^{239,240}Pu$ is given in Table 2. As expected, the vertical position and shape of $^{239,240}Pu$ peak corresponding to 1963 varies from core to core (Fig. 3). Core site 5 has the most pronounced and sharpest Pu peak at a depth of about 15 cm, while in the other cores, the Pu peaks are more diffuse. Such broad Pu peaks are indicative of physical or biological sediment mixing. Based on these down core $^{239,240}Pu$ profiles, core site 5, which is located in the most hypoxic region (Chen et al. 2001), exhibits the least amount of postdepositional alteration of the sediments.

At core site 3, located in the Mississippi River canyon at a water depth of 226 m, the $^{239,240}Pu$ peak was observed at a depth of 40 cm from the sediment-water interface. At this site, the linear sedimentation rate based on the $^{239,240}Pu$ peak, 0.82 cm yr^{-1}, is somewhat higher than the $^{210}Pb_{xs}$-based linear sedimentation rate of 0.62 cm yr^{-1}. If one uses the mass accumulation rate, which accounts for sediment compaction, both methods are in agreement ($^{239,240}Pu$ peak accumulation rate

TABLE 2. A comparison of $^{210}Pb_{xs}$-based and $^{239,240}Pu$-based linear sedimentation and mass accumulation rates in four core sites of the inner Mississippi Bight. NM = not measured.

Core	Sedimentation Rate (cm yr^{-1})		Mass Accumulation Rate (g cm^{-2} yr^{-1})	
	^{210}Pb	$^{239,240}Pu$	^{210}Pb	$^{239,240}Pu$
2	0.44	0.29	0.35	0.19
3	1.24	0.99	0.87	0.69
4	0.24	NM	0.27	NM
5	0.26	0.36	0.30	0.38

= 0.39 g cm^{-2} yr^{-1}; $^{210}Pb_{xs}$-based mass accumulation rate = 0.37 g cm^{-2} yr^{-1}; Figs. 2 and 3). The close agreement between the $^{239,240}Pu$ peak and $^{210}Pb_{xs}$-based methods confirms that there is very little vertical mixing of sediments at core site 3. This observation is consistent with earlier studies, which report that bioturbation is generally minimal in areas where sediment accumulation is fast (Crusius et al. 2004).

Mass accumulation rates within the inner Mississippi Bight can vary widely depending on the river discharge stage, position relative to the river mouth, and water depth. Observations of mass accumulation rates from the five core sites (Table 2) indicate decimeter-scale mixing processes (core site 1) to large-scale sediment focusing (core site 3). Short-term deposition rates of tens of centimeters per month during depositional periods close to the fluvial sediment source have been recently reported (Allison et al. 2000; Bianchi et al. 2002; McKee et al. 2004). Due to preferential winnowing of clastics over coarser material, finer-grained sediments are transported farther, while larger grain size sedimentary particles selectively settle out in the lower river and inner shelf sediments (Sutula et al. 2004).

SEDIMENT INVENTORY OF $^{210}PB_{XS}$, ^{137}CS, AND $^{239,240}PU$ TO INVESTIGATE SEDIMENT FOCUSING AND EROSION

In addition to providing valuable geochronological information, the inventories of particle-reactive radionuclides in sediments can also provide information on the source(s) and extent of removal of these radionuclides from the overlying water column and information on the extent of sediment focusing. Information on higher-than-expected inventories, based on regionally-defined atmospheric deposition rates of $^{239,240}Pu$, $^{210}Pb_{xs}$, and ^{137}Cs, can be used to estimate the degree of trace element contamination in sediment cores as a result of sediment focusing. The expected fallout inventory (i.e., direct atmospheric deposition) for $^{239,240}Pu$ can be calculated based on ^{90}Sr fallout measurements made in the southern region of the U.S. by the Environmental Measurements Laboratory (2006; reports, EML#415, 457, 533 and HASL-329; 1977–1991), if one assumes that the Pu activity = ^{90}Sr activity $\times$ 0.02 (Joseph et al. 1979). The expected inventory of $^{239,240}Pu$ in Columbia, South Carolina, is 0.28 dpm cm^{-2}. The corresponding inventory of ^{137}Cs (decay-corrected to 2003) is estimated to be 3.6 dpm cm^{-2}. Since the annual precipitation rate in the coastal region of the inner Mississippi Bight and Columbia are comparable (i.e., 120–150 cm), it is reasonable to assume that these inventories would result from comparable atmospheric fallout rates.

Inventories of $^{239,240}Pu$ on the sediment cores from the study site varied between 0.50 and 1.08 dpm cm^{-2} (mean value of 0.76 dpm cm^{-2}; Table 1). This range of values is significantly higher than the atmospheric fallout inventory (0.28 dpm cm^{-2}) and is comparable
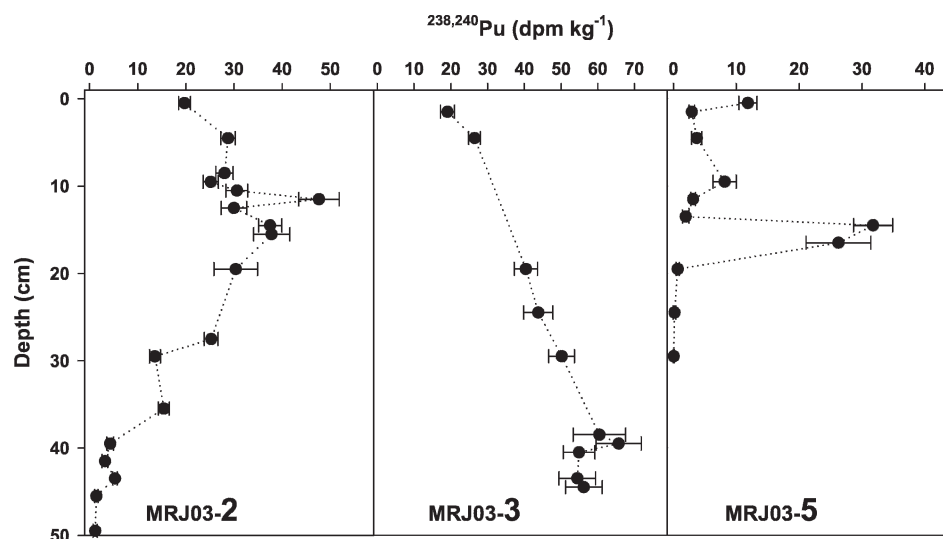

Fig. 3. Vertical profiles of $^{239,240}Pu$ activities (dpm kg^{-1}) in sediments from cores 2, 3, and 5.

to 0.97 dpm cm^{-2}, which was reported by Oktay et al. (2000) from Mississippi River delta sediments. We have similarly compared the observed inventory to that of the expected values (Table 1) to obtain the retention efficiency of these nuclides for the five core sites.

The inventories of ^{210}Pb$_{xs}$, ^{137}Cs, and ^{239,240}Pu are presented in Table 1. The source functions of these radionuclides to the sediment include direct atmospheric deposition onto the water surface and subsequent in situ removal, riverine input from erosion from the watershed, and lateral scavenging from continental shelf, slope, and open ocean waters. The ratio of the measured inventory to that derived via direct atmospheric deposition for ^{137}Cs, ^{239,240}Pu, and ^{210}Pb$_{xs}$ are also presented in Table 1. If this ratio is similar for both ^{137}Cs and ^{239,240}Pu, then it is likely that most of these radionuclides are derived from direct atmospheric deposition. It is known that Cs is generally less particle-reactive in the marine environment than Pu. If there is active scavenging within the water column, this ratio should be higher for Pu than for ^{137}Cs. At core sites 2 and 4, this ratio is the same for Pu and ^{137}Cs within 20%, suggesting that the sedimentary particles have not undergone significant water column recycling and accelerated sediment deposition due to sediment focusing has not occurred. In the case of core site 5, the ratio of the measured inventory of Pu to that of direct atmospheric deposition is considerably higher than that of ^{137}Cs, suggesting that this station, which is closest to the shore, is also influenced by localized terrestrial runoff. It is unlikely that increased scavenging alone within the water column would generate such high ratios, and we attribute these elevated ratios to accelerated sediment focusing.

Our geochronological results are similar to those of Oktay et al. (2000), who found inventories of Pu, ^{210}Pb$_{xs}$, and ^{137}Cs to be on the order of c. 200%, 330%, and 120%, respectively, of those expected from direct atmospheric deposition. One could theoretically calculate the input of watershed-derived Pu, ^{137}Cs, and ^{210}Pb by quantifying the watershed residence time of these radionuclides in terms of the watershed area. The presence of multiple reservoirs and dams on the Missouri and Ohio Rivers as well as the main stem Mississippi River makes such calculations tenuous, so we did not make any attempt to estimate the drainage input from the radionuclide data. Meade (1995) observed that the suspended sediment concentration for the Mississippi River decreased from > 900 mg l^{-1} in the early 1950s to < 200 mg l^{-1} in the 1990s due to the construction of dams and modified agricultural practices. We believe that this change in the delivery of suspended

particles does not significantly affect coastal ^{137}Cs and ^{239,240}Pu activities. Most of the Pu delivered to the ocean surface in the 1950s and 1960s would already have been removed from the surface waters, while a considerable amount of ^{137}Cs would have disappeared from surface waters due to radioactive decay (c. 60%) as well as vertical mixing of water masses. The scavenging and transport of Pu, ^{137}Cs, and ^{210}Pb in the bottom nepheloid layer remains an important, yet unresolved phenomenon (McKee et al. 2004). It is pertinent to point out that Scott et al. (1983) reported higher than expected Pu inventories in sediments collected from the Mississippi River delta. The amount of these radionuclides derived from the open ocean is unquantifiable with our present data. We can speculate that wherever the ratios of measured inventories to those of direct atmospheric deposition for ^{239,240}Pu and ^{210}Pb$_{xs}$ are higher than those of ^{137}Cs, then at those sites there is likely considerable additional inputs of ^{239,240}Pu as well as ^{210}Pb.

Trace Element Variations within Sediments

Down core trace element concentrations (Fe, Al, V, Cr, Mn, Li, Co, Cu, Ba, and Pb) for the 5 cores are available from the corresponding author. It has been shown that alumino-silicate minerals are the dominant metal-bearing phases for a large number of trace elements (e.g., As, Co, Cr, Fe, Pb, Mn, Ni, Zn, etc.), whereas Cu and Hg are thought to have a stronger covariance with natural organic phases (Windom et al. 1989; Poulton and Raiswell 2000). Most trace elements have both natural and anthropogenic source terms in coastal sediments, and the natural contribution can vary by a factor of 2 to 3, depending on the grain size distribution and concentrations of Al, Fe, Mn, and organic carbon. Even if clay minerals per se do not play a direct role in sequestering trace elements, they often act as mechanical substrates for the precipitation and flocculation of organic matter and hydrous Fe-Mn oxides (Horowitz 1991; Canfield 1997). Consequently, a strong correlation between trace element concentration and other parameters such as grain size and organic carbon has been observed in varied environments (e.g., Ravichandran et al. 1995).

Select trace element inventories (in terms of µg or mg cm^{-2}) are presented in Table 3 (down core trace element inventories are available from the author). In general, such inventories reflect not only the geographic proximity to the predominant source term (i.e., river mouth), but also provide such information relative to site-specific mass accumulation rates and sediment focusing rates. Of the studied trace elements, V, Mn, and Ba have the highest inventories per core, while Co and Cu exhibit the lowest whole core trace element in-

TABLE 3.   Select whole core trace element inventories in five sediment cores from the inner Mississippi Bight.

	Core 1	Core 2	Core 3	Core 4	Core 5
Total Core Depth (cm)	50	50	45	25	35
Cumulative mass depth (g cm^{-2})	45.91	37.9	31.23	28.09	38.62
V (mg cm^{-2})	3.48	4.78	4.24	3.24	3.92
Mn (mg cm^{-2})	31.5	27.5	52.7	18.4	17.8
Pb (mg cm^{-2})	0.97	0.99	0.96	0.52	0.68
Cu (mg cm^{-2})	0.86	0.83	0.65	0.62	0.8
Li (mg cm^{-2})	1.22	1.68	1.39	1.06	1.17
Fe (g cm^{-2})	1.13	1.45	1.23	0.88	0.96
Co (mg cm^{-2})	0.47	0.48	0.42	0.33	0.42
Cr (mg cm^{-2})	1.99	2.24	1.82	1.42	1.79
Ba (mg cm^{-2})	23.0	23.7	22.0	17.0	23.8

TABLE 4.   Correlation coefficient (r) between Al and select trace elements in five core sites of the inner Mississippi Bight.

Trace Element	Core 1	Core 2	Core 3	Core 4	Core 5
V	0.15	0.39	0.28	0.06	0.23
Pb	0.02	<0.01	0.03	0.06	0.02
Cu	0.02	0.19	0.05	0.04	0.14
Li	0.48	0.6	0.62	0.23	0.49
Fe	0.06	0.43	0.48	0.14	0.09
Co	0.26	0.28	0.29	0.24	0.28
Cr	0.34	0.67	0.36	0.1	0.45
Ba	0.36	0.04	0.12	0.13	0.04

ventories. From the concentrations of Mn in the uppermost sediments, the direct involvement of this element in redox cycling, either within the ephemerally oxygen-depleted water column or below the sediment-water interface, is evident.

NORMALIZATION OF TRACE ELEMENT CONCENTRATIONS

The pre-anthropogenic or natural concentration of trace elements can vary considerably due to variations in grain size, mineralogy, and concentrations of organic carbon, Al, Fe, and Mn (e.g., Zhang and Liu 2002). It is well known that trace elements are enriched in the finer fraction of particulates (such as the clay minerals, smectite and illite; Baskaran et al. 1984; Windom et al. 1989; Taylor et al. 1990; Horowitz 1991), while the fine-grained to coarse-grained carbonates and quartz sands are most often trace element poor phases. The two most important factors that determine the concentration of trace elements in bulk sediments are the source of the sediments and the grain size distribution (which may affect the total carbon concentration). In most environments, the natural source term of sediments remains relatively constant, leaving the granulometric parameters to be the most significant factor affecting the vertical variations of trace element concentrations. This enrichment of trace elements by the finer fraction is caused by: physicochemical sequestration, coprecipitation and flocculation of organic matter and hydrous Fe and Mn oxides, and complexation of elements onto Fe and Mn oxyhydroxides (Horowitz et al. 2001; Swarzenski and Campbell 2005).

Table 4 compares the correlation coefficient (r) between select trace elements and Al. From this subset of elements, Li and Cr exhibit the strongest correlation with Al, while Cu and Pb are only very weakly correlated. Such comparisons to Al provide information as to the origin and complexation of a wide range of trace elements transported downstream, as well as some indication as to their

respective postdeposition mobility in marine sediments. Fluctuations in down core trace element concentrations that are due principally to sand-silt-clay variations can be identified if one normalizes the data set with respect to grain size (Daskalakis and O'Connor 1995). An inherent problem with this approach lies in the quantitative separation of the finer fraction and the subsequent analyses of trace elements without altering the original concentration present in different fractions or phases. Another commonly used method to aid in the interpretation of sediment-bound trace elements is to normalize the trace element concentrations with respect to a major element of terrigenous or crustal origin, such as Al, Fe, or Ti, that most likely exhibit only a small anthropogenically-derived component (Bruland et al. 1974; Windom et al. 1989; Schropp et al. 1990; Alexander et al. 1993; Daskalakis and O'Connor 1995) or even Fe (Sinex and Wright 1988). Fe is often unsuitable because it is readily susceptible to anthropogenic influences (such as Fe sulfides and Fe oxides) and undergoes well known postdepositional redox-related transformations. Normalization with respect to Al compensates for variations in both grain size and mineralogy, because Al is representative of the quantity of aluminosilicates present, which is likely a dominant carrier phase for adsorbed trace elements. Al-normalized trace element ratios are relatively constant in undisturbed soils and the Earth's crust, and are a useful reference against which to interpret the effects of human activities (Windom et al. 1989; Schropp et al. 1990; Alexander et al. 1993). While some studies have shown little correlation between Al and select elements such as Hg (Olsen et al. 1980, 1982; Schropp et al. 1990; Coakley and Poulton 1993; Summers et al. 1996), all reported trace element concentrations were normalized to Al in this study.

ENRICHMENT FACTORS

Instead of examining the down core variation in trace element concentrations within sediments of the five core sites, we calculated and interpreted Al-normalized trace element enrichment factors

TABLE 5.   Whole core Al-normalized trace element enrichment factors (ANEF*) in five sediment cores from the inner Mississippi Bight.

Trace Element	Core 1	Core 2	Core 3	Core 4	Core 5
V	1.10 (11.7)	1.70 (18.5)	1.74 (5.11)	1.58 (4.71)	1.40 (4.12)
Mn	1.67 (2.88)	1.64 (2.90)	3.66 (6.40)	1.48 (2.69)	1.09 (1.89)
Pb	0.93 (2.74)	1.10 (3.23)	1.21 (3.62)	0.78 (2.37)	0.74 (2.22)
Cu	0.52 (2.91)	0.57 (3.22)	0.52 (2.92)	0.57 (3.31)	0.54 (3.13)
Li	0.77 (2.67)	1.21 (4.23)	1.15 (4.04)	1.04 (3.70)	0.86 (2.97)
Fe	0.69 (1.77)	1.01 (2.61)	0.97 (2.54)	0.82 (2.19)	0.67 (1.74)
Co	0.59 (1.96)	0.70 (2.28)	0.69 (2.30)	0.64 (2.19)	0.60 (2.00)
Cr	0.99 (2.73)	1.28 (3.54)	1.20 (3.32)	1.12 (3.13)	1.02 (2.85)
Ba	1.71 (1.65)	2.20 (1.97)	2.25 (2.11)	2.10 (1.96)	2.07 (1.99)

* ANEF = $(I_{te}/I_{Al})/(C_{pre-te}/C_{pre-Al})$ where I_{te} and I_{Al} represent the trace element and Al inventory, respectively, and C_{pre-te} and C_{pre-Al} represent the preanthropogenic trace element and Al concentration, respectively. Average preanthropogenic trace element concentrations were measured in six sediment intervals from a long core (> 800 yr old) collected by vibra-core within our study site. Numbers in parenthesis were calculated using upper crustal averages (Wedepohl 1995).

(ANEF), which may be defined as:

$$ANEF = [\text{trace element/Al}]_{\text{sediment sample}} \Big/ [\text{trace element/Al}]_{\text{standard material}} \qquad (4)$$

We also calculated whole core ANEF (Table 5) by substituting the inventories of trace elements and Al used in Eq. 4. In the calculation of enrichment factors (EF), the trace element concentration is usually normalized with respect to a standard material, such as average shale, a crustal reference material, or a site-specific sediment collected far below any possible influence from human activities (Santschi et al. 2001). In several earlier studies, average shale was often used as the standard material against which to interpret down core trace element distributions (Turekian 1977; Salomons and Forstner 1984). For sediment cores collected in the Sabine-Neches estuary in southeast Texas, Ravichandran et al. (1995) reported EFs to be much less than 1.0 for a suite of trace elements, such as Cr (0.3–1.2), Ni (0.4–0.86), and Cu (0.3–0.97). This implies that the shale standard might not be the most suitable reference material to calculate EFs for cores collected from that region. Ideally, several undisturbed soil cores from the drainage basin could be used to determine a mean trace element concentration. Long sediment cores that date back to a pre-anthropogenic time period could also be used as site-specific standard reference material. The caveat in this approach is that the sedimentary conditions (such as grain size and total carbon) must be uniform over the time period of interest, and the sediment source must be constant over time. In some Gulf Coast estuaries, where bottom sediments are subject to major natural disturbances, such as hurricanes, floods, and sedimentary slumps, the down core variation in trace element concentrations could be due to these episodic events, rather than to upstream anthropogenic activities (Alexander et al. 1993; Summers et al. 1996; Sutula et al. 2004). To obtain site-specific standard reference material, we used average trace element concentrations obtained from six sediment intervals of one long core (Table 6), that was collected using an onboard vibra-core platform. By extending the modeled site-specific linear sedimentation rate in these sediment cores, such depths would correspond to an age greater than 800 yr, well beyond the influence of modern anthropogenic activity. We also compared average crustal trace element values (Wedepohl 1995) and calculated corresponding EFs (Table 5, in parenthesis). Using Wedepohl's crustal abundance values as reference material, only in the case of Ba do the two approaches produce EFs of similar magnitude. This confirms the need for a local preanthropogenic reference material in sediments of the Mississippi River delta.

Whole core EFs indicate considerable enrichment for V, Mn, and Ba, while depletion was observed for Cu and Co (Table 5). Core sites 2 and 3 consistently exhibit the largest whole core EFs, while core site 1 indicates the lowest corresponding values.

HISTORICAL VARIABILITY IN TRACE ELEMENT ENRICHMENT FACTORS

The down core variations of a small subset (V, Mn, Ba, and Pb) of ANEFs for the Mississippi delta are plotted in Figs. 4–6. Whereas sediments from core site 1 were too close to the dynamic nature of Southwest Pass (Fig. 1) of the Mississippi River delta for useful geochronologies, the down core variability in EFs from this site may be used as a pseudo integrated riverine end member distribution. Core site 3 is located in relatively deep water (226 m) within the Mississippi River canyon, where $^{210}Pb_{xs}$-derived and $^{239,240}Pu$-derived geochronologies confirm enhanced sediment focusing. Within these physiographic constraints, one can interpret the sedimentary variations in trace ele-

TABLE 6. Preanthropogenic average trace element concentrations; except for Fe and Al, all trace element concentrations in $\mu g\ g^{-1}$.

	Fe%	Al%	V	Cr	Mn	Li	Co	Cu	Ba	Pb
	2.13	2.17	43	28.3	153	20.6	8.8	22.0	222	14.3
	2.51	2.37	46	30.3	227	22.8	10.0	22.8	193	14.0
	2.75	2.17	47	28.5	150	23.3	13.4	24.4	39	14.1
	2.46	2.07	46	28.1	774	22.1	12.4	24.3	213	15.5
	2.23	2.17	45	27.2	186	22.5	11.9	27.0	233	16.3
	2.27	2.36	50	30.2	170	24.8	12.0	24.4	209	16.6
Average	2.39	2.22	46	28.8	277	22.7	11.4	24.2	185	15.1

ment ANEFs. If the enrichment of trace elements were caused solely by anthropogenic discharges or emissions during a set time interval, then the ANEF peak for all elements should correspond to one sedimentary horizon that may exist at a variable depth within a core, depending on the mass accumulation rate. The vertical variability in the distribution of ^{239,240}Pu in sediments from three coring sites (Fig. 3) provides evidence for the dynamic nature in water column scavenging processes, as well as particle deposition and accumulation on the seafloor and subsequent postdepositional alterations.

Because sediment mass accumulation rates on the Mississippi Bight range from 0.27 to 0.87 g cm^{-2} yr^{-1}, different depth horizons in the sediments correspond to different calendar years. ANEFs are plotted as a function of depth, rather than date. Using modeled sediment accumulation rates, approximate calendar years that correspond to the unique EFs peaks and fluctuations are identified. Lower trace element EFs observed closer to the sediment-water interface may be the result of recent improvements in emissions controls or

regulations (Finney and Huh 1989; Ravichandran et al. 1995). Specific down core variations in select trace element EFs (i.e., V, Mn, Ba, and Pb) are discussed below.

The geochemistry of V in coastal waters may be closely tied to its redox chemistry; thermodynamics predict that it is much more soluble in oxic than reduced waters (Shiller and Boyle 1991; Shiller and Mao 1999, 2000). Removal of V from the water column is likely tied to DO concentrations on the shelf, and in the inner Mississippi Bight this is influenced foremost by the seasonality of river discharge and summertime water column stratification. Due to sedimentary removal processes, V concentrations are generally much lower in anoxic basins than in adjacent oxic seawater (Emerson and Huested 1991). Similar to Ba, V also may exhibit enrichment related to petroleum exploration and mining. The mean ANEF for V (Fig. 4) ranged from a value close to 1 (core site 1) to over 2 (core sites 3 and 5). Most scatter in EFs for this trace element was observed in core sites 2 and 3, where accumulation rates were highest. The least amount of scatter in ANEFs for V was observed at core site 5,
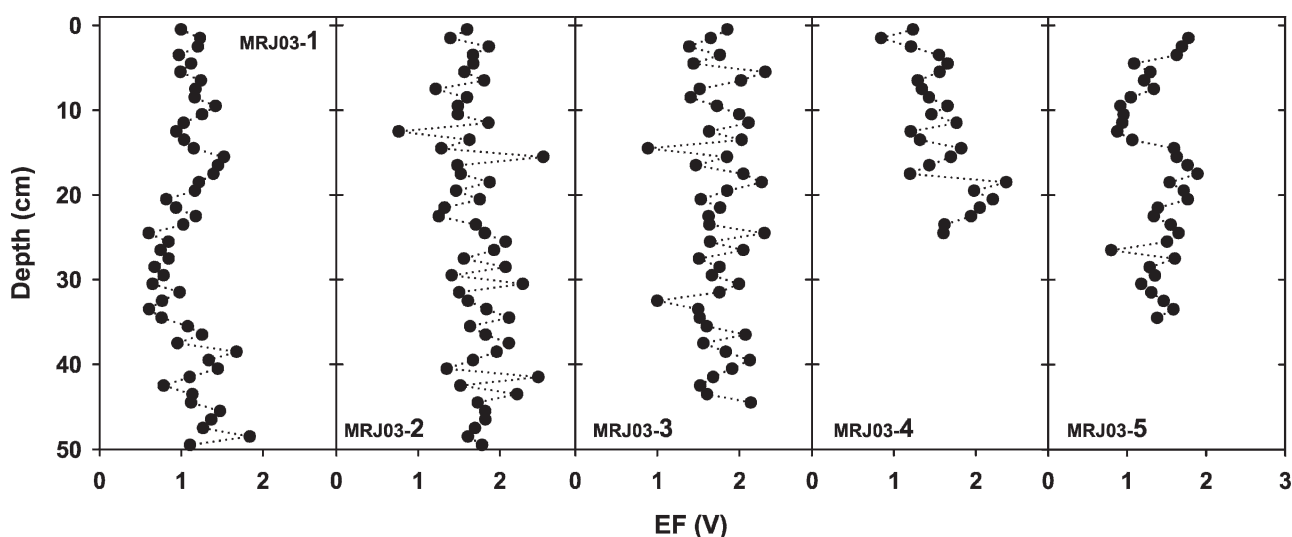

Fig. 4. Vertical profiles of Al-normalized enrichment factors (ANEF) for vanadium (V) in sediments from cores 1, 2, 3, 4, and 5. Age dates are calculated from ^{210}Pb$_{xs}$-derived mass accumulation rates.
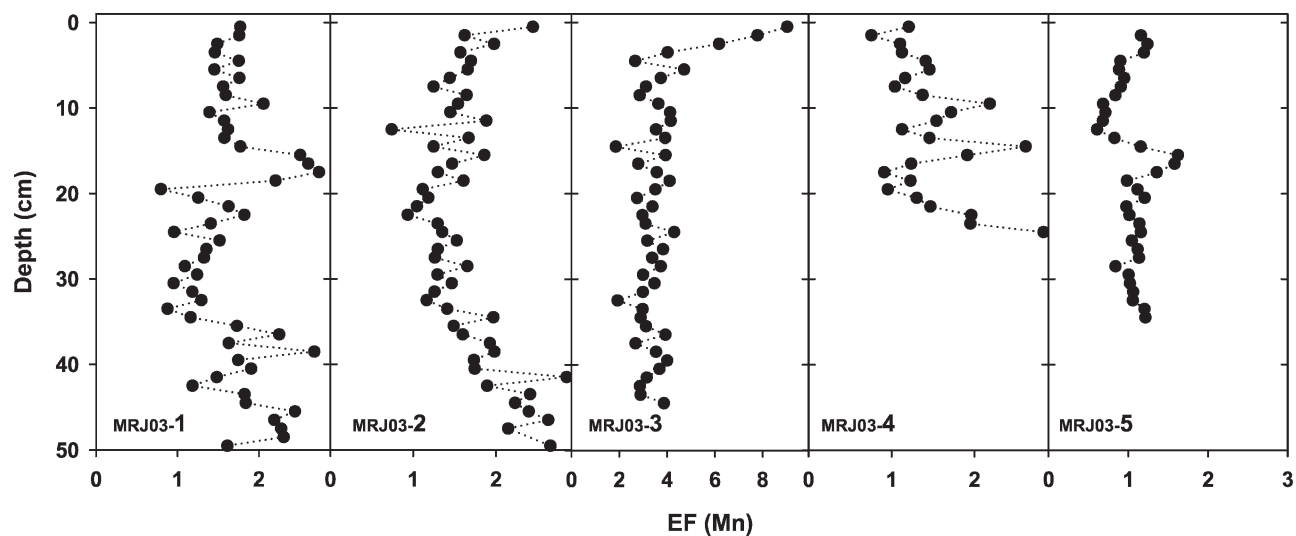
Fig. 5. Vertical profiles of Al-normalized enrichment factors (ANEF) for manganese (Mn) in sediments from cores 1, 2, 3, 4, and 5. Age dates are calculated from $^{210}Pb_{xs}$-derived mass accumulation rates.

which is located within the nucleus of what has been identified as the chronically hypoxic zone (Chen et al. 2001; Rabalais et al. 2002a,b). Such down core variability may provide evidence for seasonal redox-controlled coupling of water column removal processes (Emerson and Huested 1991) to sediment deposition or accumulation, as well as longer-term postdepositional alteration.

Mn has been of keen interest to marine scientists due to its efficient scavenging capability of particle-reactive constituents, its redox chemistry that is similar to that of Fe, and its variable sources that include continental runoff, atmospheric inputs, and redox-initiated sedimentary inputs (Trefry and Presley 1982; Balistrieri and Murray 1986; Burdige 1993; Shiller 1997a,b). The Mn distribution in sediments of the inner Mississippi Bight should reflect an integration of these various source functions within a variable depositional framework. EFs for Mn are typically greater than 1 at core sites 1–4, whereas in core site 5 the ANEFs fluctuate around a value of 1 (Fig. 5). The uppermost sediments of core site 3 exhibit very high Mn EFs, which implies enhanced redox-controlled cycling
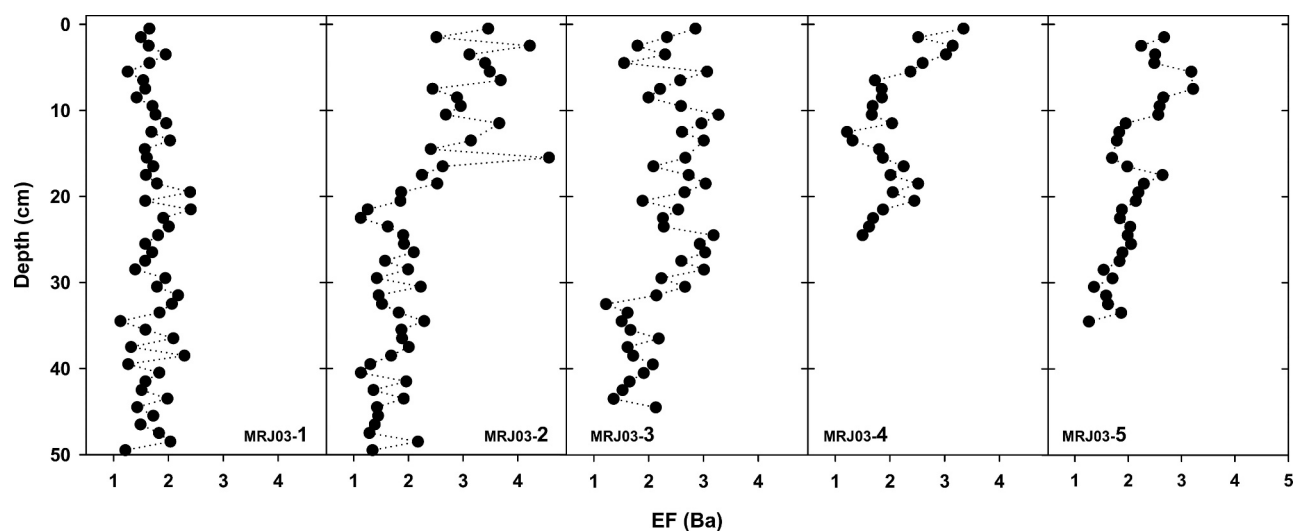

Fig. 6. Vertical profiles of Al-normalized enrichment factors (ANEF) for barium (Ba) in sediments from cores 1, 2, 3, 4, and 5. Age dates are calculated from $^{210}Pb_{xs}$-derived mass accumulation rates.

of Mn across the sediment-water interface in this core site where sediments are being effectively focused.

In marine sediments, Ba may be present in various solid phases, such as barite ($BaSO_4$), alumino-silicates, carbonates, oxyhydroxides, and organic material (Hanor and Chan 1977). Barite, the predominant Ba-bearing solid phase in the ocean, is of particular interest because it may have utility as a tracer for marine paleo-reconstructions (Broecker and Peng 1982). Barite crystals may develop in seawater by abiotic precipitation within decaying organic matter and are removed to the seafloor as aggregates. In areas of cold seep activity as well as petroleum production, such as in the northern Gulf of Mexico, discharge of Ba-rich seep fluids may also result in large in situ barite deposits. Advective transport of such precipitates from these deposits may lead to increased Ba concentrations in adjacent sediments. Analysis of ANEFs from inner Mississippi Bight sediments indicates that Ba is indeed enriched consistently in the most recent sediments of each the five cores (Fig. 6).

The down core distribution of Pb in sediments off the Mississippi River has been effectively used as a tracer of recent anthropogenic effects (Trefry et al. 1985). At a location proximal to our study site, Trefry et al. (1985) was able to identify distinct changes in Pb source terms that corresponded to declines in the use of leaded fuels. A comparable systematic decline in Pb ANEFs is observed in core site 5, although the magnitude of Pb concentrations observed at all core sites is comparable to those reported in Trefry et al. (1985) and Santschi et al. (2001).

A New Approach to the Determination of Bulk and Anthropogenic Sedimentary Trace Element Fluxes

Measurements of trace element concentrations within a geochronological framework permit the calculation of anthropogenic or bulk (anthropogenic + natural) fluxes to the uppermost sediment column. In dated sediment cores, trace element flux estimates were calculated as follows: trace element flux ($\mu g\ cm^{-2}\ yr^{-1}$) = mass accumulation rate ($g\ cm^{-2}\ yr^{-1}$) × trace element concentration ($\mu g\ g^{-1}$; e.g., Santschi et al. 1984; Ravichandran et al. 1995). This method has two potential limitations: it estimates only the present day trace element depositional flux and so cannot provide information on the historical changes in the depositional flux; and it estimates only the bulk deposition of trace elements and cannot provide information of the anthropogenic versus natural contributions. We propose a new approach for calculating the anthro-

pogenic component of trace element fluxes per whole core.

The inventory of each trace element (I_{total}) is first calculated for the entire core. The anthropogenic component (I_{xs}) for the whole core is then calculated by subtracting the inventory corresponding to the background level [= total mass depth ($g\ cm^{-2}$) × average background trace element concentration ($\mu g\ g^{-1}$)] from the total inventory of the whole core. The anthropogenic component of the trace element flux (F_{ant}) per whole core is given as:

$$F_{ant}(\mu g\ cm^{-2}\ yr^{-1}) = I_{xs}(\mu g\ cm^{-2})/t_{bot}(y) \quad (6)$$

where t_{bot} is the age of the bottommost layer in a core. Such anthropogenic trace element flux rates are compared to bulk (natural + anthropogenic) flux rates in Table 7. Using such an approach, the anthropogenic contribution for Pb varied between 16% and 103% (mean = 55%). In the case of Ba, the anthropogenic contribution consistently was in excess of 200%, suggesting that the distribution of this element is indeed affected by widespread petroleum production. Of the elements studied, Co had the lowest anthropogenic contribution (mean = 10%), implying that the source of this element is mostly natural. For Li (mean = 62%) and Cr (mean = 87%), the anthropogenic contribution is a significant component of the total depositional flux to the sediments of the inner Mississippi Bight.

Conclusions

The five core sites within the Mississippi Bight reveal a wide range in linear sedimentation rates (0.24–1.24 cm yr^{-1}) and mass accumulation rates (0.27–0.87 g $cm^{-2}\ yr^{-1}$) that reflect their respective locations relative to the Mississippi River mouth, as well as water column depth. At core site 3 located within the Mississippi River canyon, radionuclide inventories imply that sediment is effectively focused, resulting in significantly elevated mass accumulation rates. At core site 1 directly adjacent to the river mouth, the depositional environment is too dynamic to permit any useful geochronological interpretations.

From our results, we draw the following conclusions: there are wide variations in inventories of ^{137}Cs, $^{239,240}Pu$, and $^{210}Pb_{xs}$ in the five sediment cores that provide a robust framework from which one can reconstruct trace element inventories and source variations; there is good agreement in mass accumulation rates derived independently using $^{210}Pb_{xs}$ and $^{239,240}Pu$; radionuclide inventories indicate preferential and large-scale sediment focusing at select sites; of the trace elements studied,

TABLE 7.   Calculated bulk (anthropogenic + natural) and anthropogenic trace element fluxes to sediments. The first column of each core describes the bulk trace element flux, F_t = inventory of trace element/age of the core, based on $^{210}Pb_{xs}$-derived mass accumulation rates (Eq. 5). The second column describes the preanthropogenic trace element flux, F_{ant} = excess inventory of a trace element in a core/ respective age of the bottom-most layer based on $^{210}Pb_{xs}$ (Eq. 6). Numbers in parenthesis denote the anthropogenic component in percent [= (anthropogenic component/(bulk − anthropogenic component) × 100].

Trace Element ($\mu g\ cm^{-2}\ yr^{-1}$)	Core 2		Core 3		Core 4		Core 5	
V	44.1	28.0 (174)	118	77.9 (194)	31	18.7 (152)	30.5	16.6 (119)
Mn	254	157 (162)	1468	1,228 (512)	177	102 (136)	138	55.3 (67)
Pb	9.2	3.9 (74)	26.8	13.6 (103)	5.04	1.0 (25)	5.26	0.72 (16)
Cu	7.67	—	18.2	—	5.91	—	6.24	—
Li	15.5	7.6 (96)	38.7	19.0 (96)	10.2	1.8 (21)	9.09	2.3 (34)
Co	4.41	0.41 (10)	11.6	1.7 (17)	3.16	0.08 (2.6)	3.22	—
Cr	20.7	10.6 (105)	50.7	25.7 (103)	13.6	5.9 (77)	13.9	5.3 (62)
Ba	219	154 (237)	613	452 (281)	163	113 (226)	185	129 (230)

most (except Cr and Li) show a weak (< 0.5) correlation with Al; in an attempt to separate and quantify the anthropogenic trace element contribution per whole core, the calculated anthropogenic component is greater than the natural contribution for V and Ba, while for Cr, Li, and Pb, the anthropogenic contribution varied between 50% and 87%; and down core variations in Ba ANEFs reveal systematic changes that correspond to variations in both upriver and local source terms.

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