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Sediment budget-based estimates of trace metal inputs to a Chesapeake estuary

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Abstract This article evaluates whether a sediment budget for the South River, Maryland, can be coupled with metals data from sediment cores to identify and quantify sources of historic metal inputs to marsh and subtidal sediments along the estuary. Metal inputs to estuarine marsh sediments come from fluvial runoff and atmospheric deposition. Metal inputs to subtidal sediments come from atmospheric deposition, fluvial runoff, coastal erosion, and estuarine waters. The metals budget for the estuary indicates that metal inputs from coastal erosion have remained relatively constant since 1840. Historical variations in metal contents of marsh sediments have probably resulted primarily from increasing atmospheric deposition in this century, but prior to 1900 may reflect changing fluvial sources, atmospheric inputs, or factors not quantified by the budget. Residual Pb, Cu, and Zn in the marsh sediments not accounted for by fluvial inputs was low to moderate in 1840, decreased to near zero circa 1910, and by 1987 had increased to levels that were one to ten times greater than those of 1840. Sources of variability in subtidal cores could not be clearly discerned because of geochemical fluxes, turbulent mixing, and bioturbation within the cores. The sediment–metal budgeting approach appears to be a viable method for delineating metal sources in small, relatively simple estuarine systems like the South River and in systems where recent deposition (for example, prograding marshes) prevents use of deep core analysis to identify "background" levels of metal. In larger systems or systems with more variable sources of sediment and metal input, however, assumptions and measurement errors in the metal budgeting approach suggest that deep core analysis and normalization techniques are probably preferable for identifying anthropogenic impacts.

Key words Metals budget — Sediment — Chesapeake estuary

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Introduction

Numerous studies have documented elevated trace metal concentrations in sediments of the Chesapeake Bay and its estuaries (Carpenter and others 1975; Helz 1976; Goldberg and others 1978; Harris and others 1980; Sinex and Helz 1981; Nichols and others 1982; Helz and others 1985a,b; Kearney and others 1985; Delfino and Otto 1986). Identifying the sources of these elevated metal levels is critical to developing effective management strategies for reducing contamination in the bay (Marcus 1991). A common problem, however, is that identifying the source of metals in sediments is complicated by the multitude of natural and anthropogenic sediment and metal sources and the interaction of geochemical, hydraulic, sedimentologic, and biologic processes.

This article evaluates whether some problems associated with source identification can be avoided by using a detailed sediment budget to delineate and quantify metals inputs in small estuarine systems. Specifically, we examined sediment and metal inputs over a 147-year period to a small tributary estuary of the Chesapeake Bay along the western shore of Maryland.

Approaches for identifying metal sources in Chesapeake Bay sediments

Researchers have employed several approaches to identify sources of metal input to Chesapeake Bay sediments: (1) use of sediment cores to delineate historic changes due to anthropogenic inputs; (2) measurement of changes in metal concentrations in sediments with distance from major population or industrial centers; (3) use of enrichment factors to estimate the proportion of metal loading resulting from human activities; and (4) quantification of sediment and metal inputs from different sources to construct a sediment–metals budget.

Sediment cores represent an historical record of sediment and metal inputs with increased metal concentrations in the upper core generally being attributed to recent anthropogenic inputs. This technique is valuable for identifying trends, but relies on inference to distinguish the origin of metal inputs (e.g., atmospheric or fluvial). Sediment cores have been used in the Chesapeake to estimate human impacts on bay-wide metal distributions (Goldberg and others 1978; Helz and others 1985b), metal inputs to the Eastern Shore (Kearney and others 1985), industrial contributions to Baltimore Harbor (Sinex and Helz 1982), and historical trends in metal contents of tidal marsh soils (Griffin and others 1989).

Investigators have also used spatial trends in metals concentrations in surface sediments to infer the importance of anthropogenic metal inputs to the Chesapeake Bay (Harris and others 1980; Sinex and Helz 1981; Nichols and others 1982). This approach avoids the uncertainties in dating sediment cores and provides a clear portrait of regional metal distributions and probable metal source regions. This technique, however, does not identify specific pathways of metal input. Furthermore, metal distribution patterns in the Chesapeake Bay, based on monthly or annual sampling, are likely to overestimate long-term average metals inputs, because episodic floods tend to significantly lower overall metal concentrations (Helz and Sinex 1986).

Enrichment ratios have been used in the Chesapeake to distinguish human and natural metal sources in sediments, with researchers generally finding elevated metal levels near population centers along the western shore of the bay (Sinex and Helz 1981, 1982; Delfino and Otto 1986). Enrichment ratios are effective for suggesting areas of potential human impact, but do not identify specific pathways of metal input and can sometimes be misleading. If there is erosion of naturally occurring metal-rich clays, for example, enrichment ratios can suggest a pollutional metal source when in fact there is none (Hilton and others 1985).

The most obvious approach to identifying unambiguously the sources and pathways of metal inputs is to develop a budget that inventories sediment and metal inputs from different origins. Researchers have used this method to estimate metal fluxes from atmospheric deposition, coastal erosion, fluvial inputs, and geochemical mobilization to the main trunk of the Chesapeake Bay (Helz 1976; Helz and others 1985a,b) and to Baltimore Harbor (Sinex and Helz 1982).

Despite the appeal of the metal budget approach, its application is limited by the requirement for sediment and metals data from multiple sources, the errors inherent in measuring and extrapolating these data over large regions, and the difficulty of using short-term records to estimate the long-term average composition of material being delivered to estuaries. As the boundaries of the study area become smaller, however, the data requirements and errors inherent in the data should become more tractable. In addition, by coupling such a small-area budget with analysis of sediment cores and historic sediment inputs, it should be possible to estimate the long-term average composition of material being delivered to an estuary. This article evaluates whether a relatively accurate long-term sediment budget coupled with sampling of metal contents can be used to develop a reasonable quantitative portrait of metal sources and pathways to a small estuarine system.

Field area

The study area is the upper portion of the South River above Riva Bridge in Anne Arundel County, Maryland (Fig. 1). The watershed above Riva Bridge is 73 km^2 in area and sits entirely within the flat-lying sediments of the Maryland Coastal Plain. Tributary streams primarily drain the Aquia Formation, a glauconitic sandstone that is clean to moderately argillaceous and calcareous (Maryland Geological Survey 1976). The shoreline consists of tidal marshes near creek mouths, beaches in embayments, and bluffs ranging up to 35 m in height. Water depths average about 1.2 m and never exceed 6.6 m. The study area is in the oligohaline and upper mesohaline portion of the estuary, which minimizes complications associated with multilayered transport of material typical of mixing zones in estuaries (Förstner and Wittmann 1983).

In 1985, 57 percent of the land cover in the watershed was forest, 25 percent was residential, and the remainder was largely agricultural (McWilliams 1977). Since European settlement, much of the originally forested landscape has been repeatedly cleared for agriculture or timber and then abandoned to revert to forest. The percentage of land cleared for agriculture probably peaked between 40 and 50 percent around 1840 (Brush 1984).

Regional sources of metal loadings in the upper South River are Annapolis, which is 3 km to the east, Baltimore, which is 50 km to the north, and Washington, D.C., which is 50 km to the west. Annapolis is mainly an administrative, commercial, and residential area with 35,000 residents and a population of some 250,000 within a 15-mile radius. With the possible exception of Honeywell Industries in a tributary of upper Broad Creek (Fig. 1), there is no industrial discharge into streams in the study area. In the watershed and estuary, the only obvious sources of heavy metals in the recent past are automobile emissions, highway runoff, domestic effluents, and boat traffic.

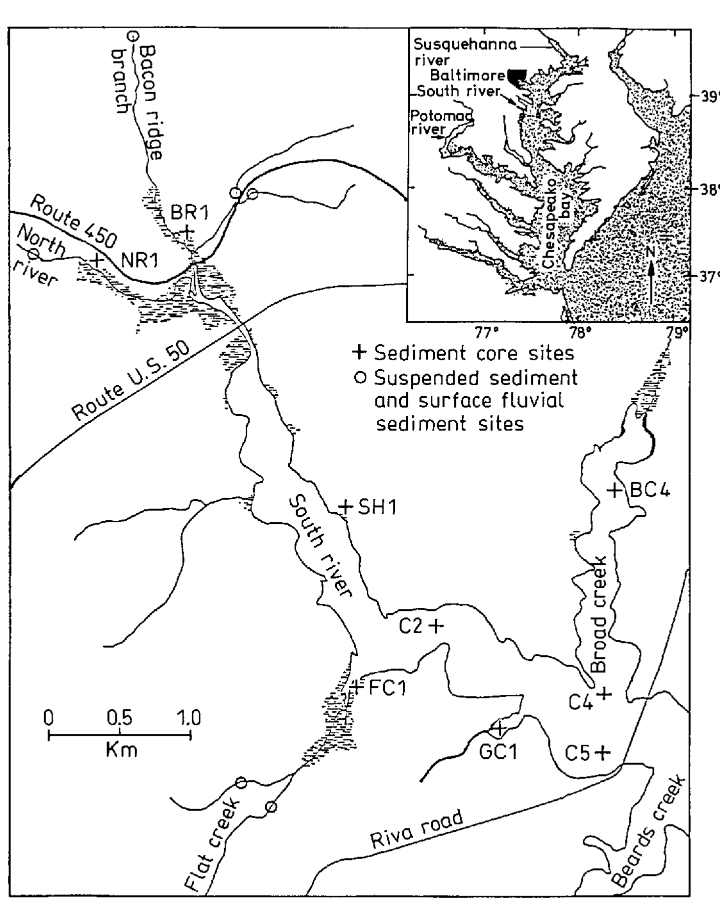

Fig. 1. The South River estuary, Maryland, and location of sediment and metal sampling sites. Crosses indicate core sites and circles mark river sampling sites

Methods

A budget of metal inputs, storage, and exports was compiled by combining an existing sediment budget for the upper South River with new metals data for surface sediments and cores. The methods used to determine the sediment portion of the budget are reported in detail in Marcus and Kearney (1991) and are only briefly summarized here.

The sediment budget for the upper South River above Riva Bridge covers the period between 1846 and 1970. Marcus and Kearney (1991) estimated a range of probable long-term fluvial inputs based on monthly sampling of high flow events in the watershed and on a continuous ten-year record of sediment loads at the Smithsonian Environmental Research Center in the adjacent Rhode River watershed (Pierce and Dulong 1977; Correll, Jordan and Pierce, unpublished data). The areal extent of marsh progradation and volumetric sediment inputs from shoreline erosion were calculated from shoreline positional changes shown on maps or aerial photographs from 1846, 1903, 1933, and 1970. Sediment storage was estimated from cores collected in tidal marshes and subtidal sediment (Fig. 1). Marcus and Kearney (1991) used changes in oak–ragweed pollen ratios to estimate sedimentation rates in tidal marsh cores and ^{210}Pb dating and changes in subtidal bathymetry to estimate subtidal sedimentation rates. In order to expand the Marcus and Kearney data set and verify their calculated sedimentation rates, this study includes new ^{210}Pb data for three marsh cores and two subtidal cores.

Metal concentrations required for the budget were measured in: (1) the marsh and subtidal cores; (2) fluvial bed sediment; and (3) cliff sediment. Cliff sediment samples were collected at 12 locations that had experienced active erosion. Fluvial bed sediment sediment samples for metals analysis were collected at seven locations (Fig. 1).

The trace metals chosen for analysis were Pb, Mn, Cu, Zn, and Fe. Iron, and Mn often provide a good indication of the role that absorption/desorption processes play in controlling trace metal concentrations. Copper, Zn, and Pb are usually associated with industrial and residential activities in watersheds and airsheds. Sediment samples were analyzed for metal content using the hot nitric and hydrochloric acid digestion procedure outlined by Evans and Rigler (1980). This digestion is a relatively harsh one, which only leaves behind trace metals associated with silicate minerals. The supernatant was analyzed by atomic absorption spectrophotometry.

The organic content and silt/clay content of sediment samples were measured to determine the influence of these factors on metal concentrations. Organic contributions to the sediment budget were determined by weight loss on ignition at 475°C for 4 h using techniques outlined by Ball (1964). The percentage of each sediment sample that was sand or silt and clay was determined by wet sieving.

Sediment and metals data

Table 1 shows estimated annual sediment inputs from cliff erosion and rivers from 1846 to 1903, 1903 to 1933, and 1933 to 1987, which are the dates corresponding to topographic map and aerial photo coverage. Annual rates of marsh and subtidal deposition at the individual core locations are shown in Table 2. Marsh accumulation rates based on pollen dating represent the period from approximately 1840 to 1987. Pollen was not preserved in the subtidal cores and could not be used as a dating technique at those locations. The subtidal core ^{210}Pb-based accumulation rates are the average for approximately 100 years prior to 1987 when the cores were collected. The ^{210}Pb rates in three instances generally agree with bathymetry-based rates for the period 1903 to 1933, the last date when bathymetric maps of the site were compiled (Table 2). In one case the rate differs by almost a factor of two and for four cases no comparison was possible.

The complete metals data set for the marsh and subtidal cores is reported in Nielsen (1990). Average metal concentrations in sediments from the 12 eroding cliff sites and seven river sites are reported in Table 3. We used regression analysis to examine the relationship of Pb, Cu, and Zn concentrations to organic content, silt/clay content, and Fe concentrations in separate depositional environments (Table 4). The relationships were weak to nonexistent or could not be generalized across depositional environments and did not justify normalizing metal concentration data in subtidal and marsh cores to account for scavenging effects of organics, clays, or iron.

Table 1. Rates of sediment input (megagrams/year) to the South River estuary from rivers and cliff erosion[a]

Source	1948–1903	1904–1933	1934–1987
River	2,837	2,837	928
Cliff Erosion	13,959	12,484	6,606

[a] Based on data from Marcus and Kearney (1991)

Table 2. Marsh and subtidal sediment mass accumulation rates (g/cm^2-yr)[a]

Core	Pollen-based accumulation rate (1840–1987)	^{210}Pb-based accumulation rate (1887–1987)	Bathymetry-based rate (1903–1933)
Marsh core NR1	NA	0.64	NA
Marsh core BR1	NA	0.92	NA
Marsh core FC1	0.41	0.36	NA
Marsh core SH1	0.47	NA	NA
Subtidal core C2	NA	0.29	0.23
Subtidal core C4	NA	0.39	0.72
Subtidal core C5	NA	0.45	0.36
Subtidal core BC4	NA	0.61	0.53
Subtidal core GC1	NA	NA	0.55

[a] Starting dates for the pollen and ^{210}Pb-based accumulation rates are approximate. Pollen and bathymetry results based on data from Marcus and Kearney (1991)

Table 3. Average metal concentrations in river and cliff sediments used to construct the sediment–metal budget[a]

	Pb (μg/g)	Cu (μg/g)	Mn (μg/g)	Zn (μg/g)	Fe (mg/g)
Cliff					
Avg.	7.9	3.5	99.0	22.8	43.6
n	12	12	12	12	12
SD	2.8	1.4	64.9	17.4	20.1
River					
Avg.	5.5	2.2	65.5	15.8	24.4
n	7	7	7	7	7
SD	1.7	0.9	31.5	5.6	8.0

[a] River sediment collection sites are shown by crosses in Fig. 1. The 12 cliff samples were spaced approximately equidistantly along the shoreline of the South River and Broad Creek above Riva Bridge. All samples were collected in June and July of 1989

Table 4. R^2 values for correlations of organic content, silt/clay content, and Fe concentrations (x) with Pb, Cu, and Zn concentrations (y) in the South River, Maryland

Location	Metal	Sample size	Silt and clay (%)	Organic content (%)	Iron concentration (mg/g)
Marsh and subtidal sediments	Pb	126	0.03	0.10	0.00
	Cu	126	0.06	0.08	0.00
	Zn	126	0.02	0.01	0.29
Cliff sediment	Pb	12	0.00	NA	0.75
	Cu	12	0.55	NA	0.00
	Zn	12	0.06	NA	0.76
River sediment	Pb	7	0.48	NA	0.64
	Cu	7	0.04	NA	0.13
	Zn	7	0.01	NA	0.20

Construction of the sediment–metals budget

Construction of the sediment–metals budget required partitioning inputs for different dates at each core site between river sediment, sediment from eroding shoreline, and residual metal deposition (which includes atmospheric deposition). Sediment from the main trunk of the bay was not included as an input because it does not enter the upper portions of the South River estuary where the cores were collected.

Deposition rates at marsh and subtidal core sites were assumed to be constant. This allowed us to assign approximate dates to different depths within the cores using the equation:

$$\text{Date} = 1987 - d/R \tag{1}$$

where d is the depth in centimeters and R is the rate of deposition in centimeters per year.

Marsh budget

Because of their location, all sediment in the tidal marshes is derived from fluvial deposition and there are no sediment inputs from coastal erosion. The rate of fluvial sediment input to a marsh site is therefore equal to the mass rate of sediment deposition at that marsh site (D_m) in grams per square centimeter per year (Table 2). The fluvial metal loading (L_{mf}) to marshes in micrograms per square centimeter per year is therefore:

$$L_{mf} = D_m * C_f \tag{2}$$

where C_f is the concentration of metals in fluvial sediment in micrograms per gram. No data are available for historical metal concentrations in fluvial sediment, so C_f for the metal budget prior to 1987 was assumed to be equal to modern day average concentrations (Table 3). This is probably a reasonable assumption given the homogenous geology and absence of any industrial activities within the basin. Because of the assumption of constant sediment deposition rates and constant fluvial metal concentrations through time, equation 2 generates only one value for fluvial metal loading to marshes for each metal (Table 5).

The total marsh metal loading (L_m) for a given date is:

$$L_m = D_m * C_m \tag{3}$$

where C_m is the metal concentration in marsh sediment for that date. The residual metal loading (L_{mr}) not accounted for in this budget probably primarily represents atmospheric metal deposition with other sources and factors playing a more minor role. Atmospheric deposition may thus be estimated from:

$$L_{mr} = L_m - L_{mf} \tag{4}$$

Figure 2 shows atmospheric loading at four sites for Pb, Cu, and Zn.

Table 5. Budget estimates of fluvial metal contributions to marshes and fluvial and coastal metal contributions to subtidal sediments

Core	Period of loading[a]	Flvuial inputs Pb	Flvuial inputs Cu	Flvuial inputs Zn	Coastal inputs[b] Pb	Coastal inputs[b] Cu	Coastal inputs[b] Zn
Marsh core NR1	1917–1987	3.5	1.4	10.1			
Marsh core BR1	1927–1987	5.0	2.0	14.5			
Marsh core FC1	1840–1987	2.3	0.9	6.6			
Marsh core SH1	1840–1987	2.6	1.0	7.4			
Subtidal core C2	1934–1987	0.2	0.1	0.6	2.0	0.9	5.8
	1904–1933	0.3	0.1	0.9	1.9	0.8	5.4
	1887–1903	0.3	0.1	0.9	1.9	0.8	5.4
Subtidal core C4	1934–1987	0.3	0.1	0.8	2.7	1.2	7.7
	1922–1933	0.4	0.2	1.1	2.5	1.1	7.2
Subtidal core C5	1934–1987	0.3	0.1	0.9	3.1	1.4	9.1
	1904–1933	0.5	0.2	1.3	2.9	1.3	8.4
	1880–1903	0.4	0.2	1.2	3.0	1.3	8.6
Subtidal core BC4	1937–1987	0.4	0.2	1.2	4.2	1.9	12.1
Subtidal core GC1	1973–1987	0.4	0.1	1.1	3.8	1.7	10.9

Amount ($\mu g/cm^2$-yr)

[a] Earliest date is determined by the depth of the core. The periods 1934–1987, 1904–1933, and prior to 1903 correspond to the periods for which sediment inputs from rivers and cliff erosion are available (Table 1)
[b] Sediments and associated metals eroded along shorelines were not deposited in tidal marshes

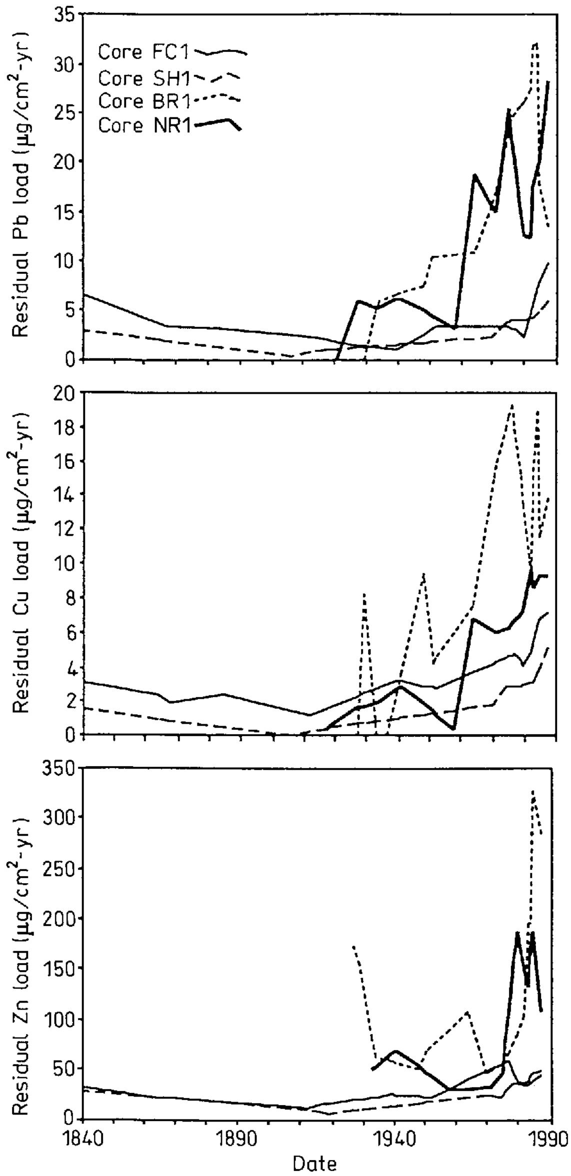

Fig. 2. Residual metal loading not accounted for by river inputs in tidal marshes of the South River, Maryland. Atmospheric deposition is probably the primary source of residual metal loading in marsh sediment after 1900

Subtidal budget

Subtidal sediment derives from both fluvial and shoreline erosion. No direct data are available to indicate the proportion of sediment from each source that has been deposited at individual core sites through time. We therefore assumed that the quantity of sediment from each source deposited at a site was in direct proportion to the amount of erosion from each source. The mass rate of fluvial sediment deposition (D_f) at each site in a given year in grams per square centimeter per year is therefore:

$$D_f = D_s * Q_{sf}/(Q_{sc} + Q_{sf}) \tag{5}$$

where D_s is the subtidal sediment deposition rate at a given core in grams per square centimeter per year. Q_{sf} is the annual fluvial sediment input to the estuary for that date, and Q_{sc} is the annual coastal sediment input to the estuary for that date, both in megagrams per year (Mg/yr). Values for Q_{sf} and Q_{sc} for different dates are shown in Table 1.

Similarly, the mass rate of coastal sediment deposition D_c in grams per square centimeter per year at each core site in a given year is:

$$D_c = D_s * Q_{sc}/(Q_{sc} + Q_{sf}) \tag{6}$$

Fluvial contributions to subtidal metal loading (L_{sf}) in micrograms per square centimeter per year for a given date are:

$$L_{sf} = D_f * C_f \tag{7}$$

and the coastal contributions to subtidal metal loading (L_{sc}) in micrograms per square centimeter per year for a given date are:

$$L_{sc} = D_c * C_c \tag{8}$$

where C_c is the average concentration of a metal in coastal sediment (Table 3). We assumed that metal concentrations in eroding shore sediment remained constant through time, which is likely given the homogenous geology of the eroding shore faces. Table 5 shows the budget estimates of subtidal metal loading from rivers and shoreline erosion based on equations 5–8.

The total subtidal metal loading (L_s) for a given date is:

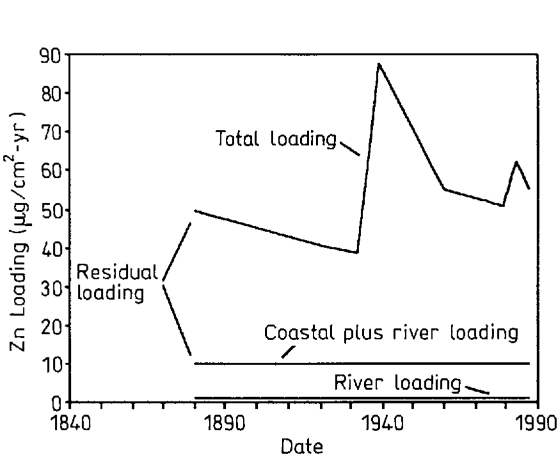

Fig. 3. The different components of Zn loading in subtidal sediment, core C5, South River, Maryland. The large majority of variation in total metal loading in this and other cores for all metals is due to variations in the residual load

$$L_s = D_s * C_s \tag{9}$$

where C_s is the metal concentration in the subtidal core corresponding to that date. The residual subtidal metal loading (L_{sr}) unaccounted for in this budget is:

$$L_{sr} = L_s - L_{sf} - L_{sc} \tag{10}$$

Figure 3 provides a graphical portrayal of the results of these calculations for core C5 for Zn. Although changes in calculated river and coastal metal loading do occur through time, the changes are very minor compared to variations in total subtidal metal loading at the site. This was typical of all the sites and did not change noticeably

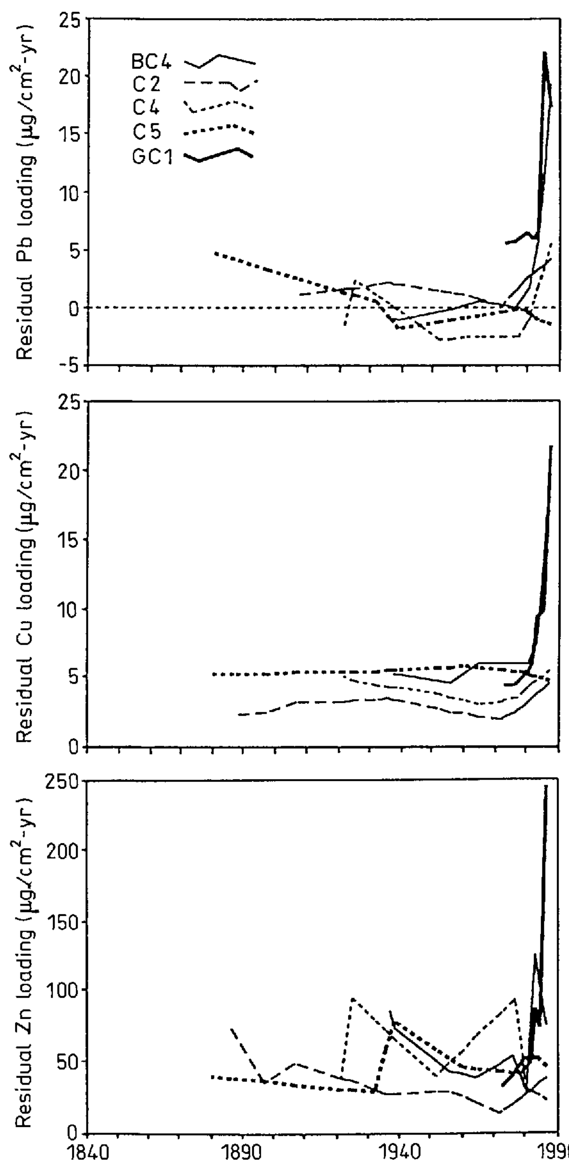

Fig. 4. Residual metal loading in subtidal sediment of the South River, Maryland. Variations in residual metal loading in subtidal cores represent a complex mix of historic variations in metal inputs combined with the effects of mechanical sediment mixing, bioturbation, and geochemical fluxes