

Accumulation of muds and metals in the Hudson River estuary turbidity maximum

M. G. Menon · R. J. Gibbs · A. Phillips

Abstract In the Hudson River estuary, fine mud and toxic metals are enriched in the upstream turbidity maximum. The mechanisms causing the enrichment were assessed through the analysis of suspended-sediment concentration (SSC) (bottom and surface), particle size, and trace metal distributions. Bottom SSCs varied across the study area by a factor of ten, and the turbidity maximum activity was observed in between kilometers 45 and 80. The particle-size analysis defined two accumulation modes: <4.65 and $>22.1 \mu\text{m}$. The ratio of the fine-to-coarse mode increased from 1.75 to 2.75 in the turbidity maximum. The fine mud concentration (55–60%) in the turbidity maximum was found to have a high correlation ($r=0.98$; $p<0.005$) with the concentration of $<2\text{-}\mu\text{m}$ particles. A conceptual model was derived in order to understand the possible mechanisms by which fine mud (and specifically $<2\text{-}\mu\text{m}$ particles) is concentrated. The two dominant size modes were analyzed for toxic metals. The upstream tributaries are major sources of metals compared to point sources at downstream locations. In the turbidity maximum, Cd, Cu, Zn, and Pb are significantly enriched compared to average shale metal values and ERM toxicity guidelines by 580, 42, 10, 16 and 12, 7, 2.4, 1.4 times, respectively. Decreasing metal concentrations downstream of the turbidity maximum imply that Haverstraw Bay acts as temporary storage for fine particles and enriched metals. It is demonstrated in this study that toxic metals are enriched in Haverstraw Bay due to the mud accumulation. The high levels of toxic metals in the sediments of the Hudson River estuary are a major concern because hu-

man activities (dredging and river traffic) cause re-suspension of sediments and can change the mobility patterns of bioavailable contaminants.

Key words Hudson River · Estuary · Heavy metals · Turbidity maximum · Mud

Introduction

Identifying specific processes responsible for trace-metal remobilization and bioavailability helps us to understand the dynamics of trace metals in estuaries (Sanders and Riedel 1992). Previous studies have demonstrated that trace metals in the fluvial systems are mostly transported in association with suspended sediments (Gibbs 1977; Windom and others 1984; Meybeck and Helmer 1989; Horowitz 1991; Gibbs 1994). Quantification of such processes is a prerequisite for geochemical mass balances, prediction of the fate of contaminants (Turner and others 1993), and understanding trends in point and nonpoint sources of pollution (Forstner and Wittman 1981; Meybeck and Helmer 1989; Horowitz 1991). Estuaries are areas of sediment accumulation because of decreasing flow velocities and the resulting aggregation of fine particles (Gibbs 1987). The deposited sediments can be resuspended and contaminant adsorption/desorption cycles can set in with changing physico-chemical conditions (Sanders and Riedel 1992). Sedimentation, temporary storage, and resuspension of sediments constitute an important loop in the contaminant pathway that is often overlooked. Fine sediments and associated metals in the estuary may either be accumulated or removed depending upon the mechanisms creating a turbidity maximum. Temporal variation of discharge is one of the major contributing factors in the distribution and transport of metals (Presley and others 1992; Broman and others 1994). Investigations of the metal behavior in the Delaware River estuary turbidity maximum (Biggs and others 1983) demonstrated a maximum association of metals with particulate phases at points of low salinity, and the region of moderate salinity has low metal concentrations. This was attributed to the dilution of contaminated particulates by resuspended uncontaminated bottom sediments which

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are transported landward by flood tidal currents. The upstream transport of sediments during flood tides and the consequent trapping is well studied (Jay and Musiak 1994). During this process flood tides bring in coastal derived uncontaminated sediment that mix with contaminated fluvial derived sediments (Forstner and Wittman 1981). In the case of the Hudson River estuary, metals have been deposited for years in the lower regions of the estuary in association with the fine sediments and are re-lected as high particulate (Klinkhammer and Bender 1981) and bottom sediment metal concentrations (Gibbs 1994). The high metal content is related to the fine particle size of the sediment (Ellsworth 1986) and the metal inputs from various sources (Bero and Gibbs 1990). Ellsworth (1986) concluded in his study that the tributaries, in situ biological production, and the input from the sea could account for the fine sediments in the lower Hudson River. Thus tidal oscillations and resuspension of sediments become important in terms of remobilization of toxic metals in the Hudson River estuary.

The turbidity maximum in the Hudson River estuary usually exists slightly downstream of the salt front, depending on circulation and bed erodability. Changes in the channel bottom configuration (Cooper and others 1988) between locations at kilometers 45 and 80 in the estuary may be responsible for the resuspension of bottom sediments. Bokuniewicz and Arnold (1984) identified a second turbidity maximum near George Washington Bridge, at kilometer 19. These two turbidity maxima are probably temporary storage for sediments which are later resuspended and disaggregated and the fine particles subsequently transported to New York Harbor. This could explain high sedimentation of fine particles (Olsen and others 1978) and high metal concentrations in New York Harbor (Gibbs 1994).

The present study focuses on the chemical composition of the sediments and mechanisms determining the metal-sediment accumulation in the turbidity maximum between kilometers 45 and 80 from the Battery, New York.

Study area

The Hudson River originates at Lake Tear in the Adirondack Mountains of northern New York and flows 507 km south to the Atlantic Ocean. North of Albany the Mohawk River, a major tributary (Fig. 1), joins the Hudson River. Several smaller tributaries enter the Lower Hudson River from the mountains and highlands downstream of Albany. The Upper Hudson and the Mohawk watersheds (25927 km²) contribute approximately 80% of the annual freshwater (Cooper and others 1988) and 98% of the sediments (Water Resources Data 1977) to the lower Hudson. Monthly discharges are highest in spring and fall because of snowmelt and heavy rainfall, respectively. The salt front in the Hudson River estuary migrates between Poughkeepsie (Fig. 1, at km 120) and the Tappan Zee bridge (at km 45) depending on flow conditions.

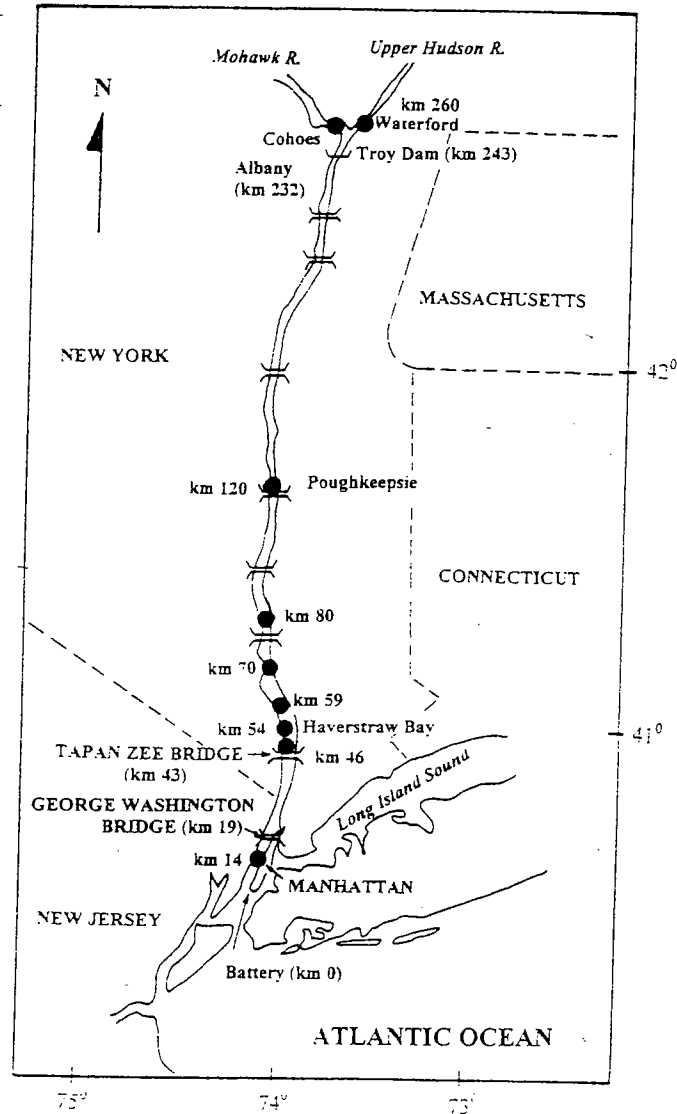


Fig. 1 Map of the Hudson River and sampling sites (●) with distances (km) from the Battery, New York

Methods

Sample collection

The suspended-sediment samples were taken in 2-l bottles from 20 cm below the surface and 1 m above the bottom on 8 October 1993 using a fast boat travelling upstream. The sampling locations are shown in Fig. 1. Depth integrated samples were collected from four locations (km 46, at Hastings; km 120 at Poughkeepsie; km 260 at the Mohawk River and the Upper Hudson River) by the United States Geological Survey (USGS) on 11 October 1993. Bottom and surface suspended samples collected during the 1991 study (Gibbs 1994) were also mentioned for discussion purposes. The samples were collected in acid-cleaned, low-density, polyethylene bottles that were cleaned by soaking in 33% HCl at 60 °C for

48 h and rinsing with distilled, deionized water which had been tested for trace metals. Blank filters were analyzed for trace metals. The water samples were filtered through 0.45- μm cellulose nitrate membranes in a clean area. The filter membranes with the sediments and blanks were washed with 10 ml of deionized water to remove salts. The filtrate was retained and oven-dried overnight at 60 °C.

Trace metal analysis

Total recoverable metals of the particulates were determined by following Environment Protection Agency (EPA) method 200.7 (Martin and others 1992). Method 200.7 is useful in extracting the bio-available fraction of the contaminants associated with sediments. The total digestion using HF breaks down the crystal structure of particles. The total metal content (which also includes the metals within the crystalline structure) will not reflect the bio-available metal levels under the normal riverine and estuarine environmental conditions. It is found that method 200.7 efficiently extracts metals associated with major geochemical phases and is thus preferred over total digestion. The suspended-sediment samples with filter membranes were transferred to 250-ml Phillips beakers and digested in 4-ml (1:1) HNO_3 and 10-ml (1:4) HCl. The samples were heated on a hot plate and refluxed for 30 min. Vigorous boiling was avoided to prevent the loss of HCl- H_2O azeotrope. The samples were allowed to cool and were transferred to 100-ml volumetric flasks and diluted to known volumes with deionized, distilled water. Insoluble materials were separated by centrifuge. The trace metals in the sample solutions were determined by utilizing techniques for simultaneous and sequential multi-element determinations with a Jobin-Yvon (JY 70 Plus) Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES). For quality assurance blanks were carried out throughout all stages of sample collection and analysis. The samples were measured for trace metals in triplicate and measurements were repeated if standard deviations exceeded 10%. Blank analyses were conducted to measure the metals in distilled water, reagents, and filters and were found to be very low relative to sample concentrations. A multi-element plasma standard from Spex Industries, Edison, New Jersey, with quality control 19 was utilized (Gibbs 1994). Mid-range control standards were analyzed every sixth sample. The detection limits were set according to the EPA method 200.7 (Martin and others 1992).

Particle size analysis

The primary particle-size analysis was performed on suspended-sediment samples with a custom-made particle-size analyzer which measures settling velocity based on optical principles reviewed by Jordan and others (1971). This particle-size analyzer has high-resolution narrow beam optics, short-wavelength monochromatic light, and controlled temperature. The sediments on splits of filtered samples were disaggregated with an ultrasonic probe and resuspended in 1% sodium hexametaphos-

phate. Every tenth sample was analyzed twice to verify accuracy and precision. The instrument analyzes small quantities of sediments with high resolution, especially bimodal distributions. The sedimentation analysis (Atterberg) and sedigraph could not be used, since these systems utilize relatively large quantities of sediments. Laser-based instruments do not give the resolution needed to meet the criteria of this study, to analyze two accumu-

Results

Suspended-sediment concentration (SSC)

Parts a and b of Fig. 2 show high concentration of bottom suspended sediments between km 46 and 80 in the Haverstraw Bay. The minimum average SSC between km 45 and 80 was 40 mg/l during the 1991 sampling. The high bottom SSC in this region is the result of estuarine turbidity maximum activity. During 1993 sampling, bottom SSCs between km 13.5 and 120 vary by a factor of 10 (Fig. 2a) and 1991 sampling showed more than ten times spatial variation in SSC. The variations between 1991 and 1993 sampling are probably due to seasonal discharge conditions. This upstream turbidity maximum activity is fueled by resuspension of available sediments at the bottom of the Haverstraw Bay.

Particle size distribution

Primary particle-size analysis of the suspended sediments reveals a bimodal grain-size distribution. The dominant finer-size mode comprises particles mainly < 4.65 μm and the dominant coarser mode comprises particles mainly 22.1–63 μm (Fig. 3a). Hereafter, the < 4.65 and the 22.1–63 μm fractions will be referred to as fine and

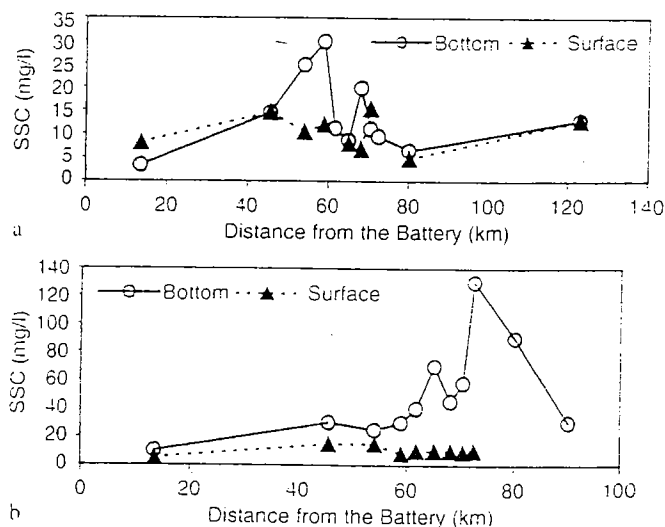


Fig. 2a, b

The bottom (○) and surface (▲) suspended-sediment concentration of the Hudson River estuary, a present study and b Gibbs (1994) study

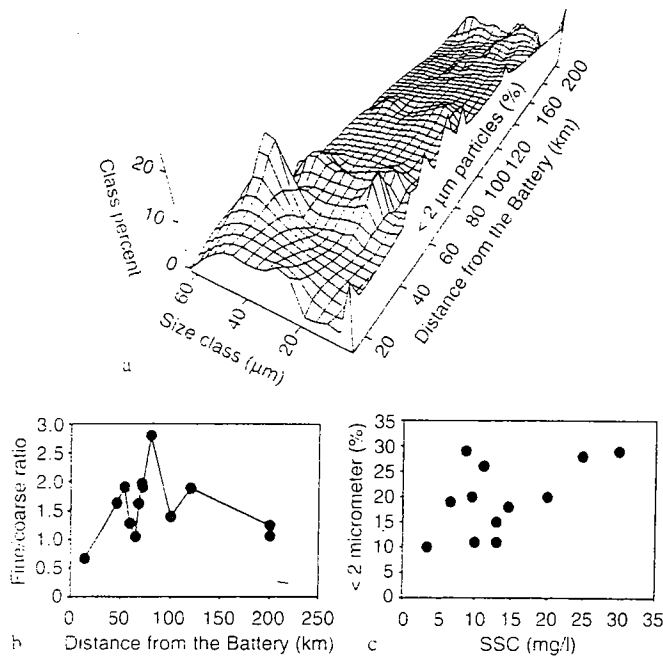


Fig. 3a

Spatial primary particle-size distribution of bottom suspended sediments, b fine-to-coarse ratio with distance (km) from the Battery, New York, and c correlation between percent <2 μm and suspended-sediment concentration (mg/l)

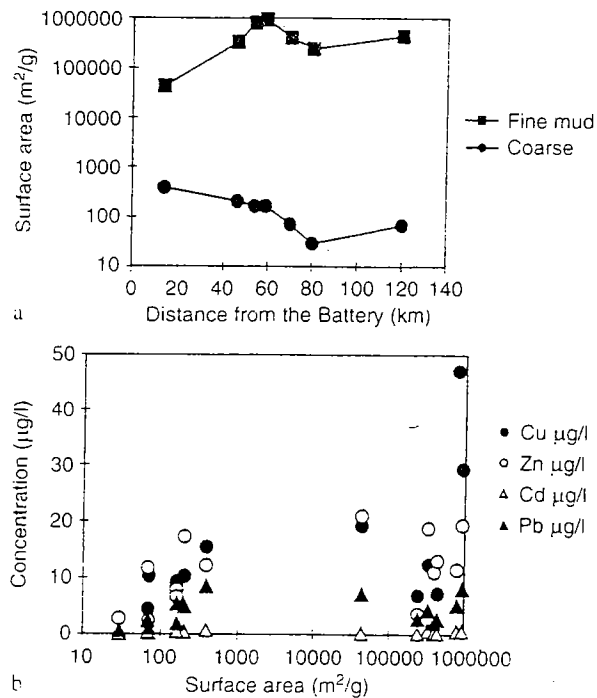


Fig. 4a

Calculated surface area for the fine fraction (<7.8 μm) and the coarse fraction (>7.8 μm) of the bottom suspended sediments, and b accumulated heavy metals and the surface-area relationship in the bottom suspended sediments

coarse, respectively. The Upper Hudson and the Mohawk Rivers are the main sediment sources for Haverstraw Bay. The samples from these tributaries were also compared with the Haverstraw Bay sediment samples. The Upper Hudson River at Waterford and Mohawk River at Cohoes have similar particle-size distributions (Fig. 3a, km 260). The clay size population (<2 μm) of both tributaries is 11%. The 2–13- μm distributions in the sediments of the Mohawk River and the Upper Hudson River are similar. The particle-size distributions of the two tributaries are not retained in the locations downstream, though these tributaries are the major source of the particles. At Poughkeepsie (km 120), the coarse-size fraction decreases and as a result the clay fraction increases from 11% to 26%. It is likely that the coarser silt may be deposited behind the dam at Troy, or along the river course, leaving the finer population to be carried down river. Thus, the fine-to-coarse ratio increases in Haverstraw Bay and the highest ratio is found in the at km 80 (Fig. 3b). The near-bottom suspended sediment in the turbidity maximum consists of 50% to 62% fine particles mostly of sizes <2 μm (significant positive correlation between percentages of mud and <2 μm , $r=0.98$; Fig. 3c). The increase in the fine particles especially those <2- μm , in the turbidity maximum is crucial in terms of increased contaminants due to high surface areas, and also the higher levels of bioavailable metals found on particle surfaces. The surface areas were calculated (Gibbs 1994) for <7.8- μm and >7.8- μm fractions. Shapes of particles less than

3.5 μm in diameter were assumed to be rectangular with thickness H one fifth of the length L . Particles larger than 3.5 μm were assumed to be cubes. By assuming a particle density (ρ) of 2.6 g cm^{-3} , the surface area of the sample materials were calculated as: $A = C_s [\rho L W H]^{-1}$ of each size fraction, where C_s is the SSC. The total surface area of the fine fraction is an order of magnitude greater than the coarse fraction in Haverstraw Bay (Fig. 4a). Towards the ocean, the ratio of fine to coarse decreases due to the coastal sediment flux of sand (Gibbs 1994).

Metal distribution

The effective fining of particles coming into Haverstraw Bay and the increasing surface area of those particles resulted in an increase in the particulate metal content in the Haverstraw Bay (Fig. 4b). The concentrations of metals like Cu, Zn, Cd, and Pb are highest within the turbidity maximum, and Ni, Cr, and Fe show no enrichment. The concentration levels of enriched metals in the suspended sediments (<63 μm) from upstream and downstream of turbidity maximum are in the same range (Fig. 5c). The enriched metals in the <7.8- μm fraction of the bottom suspended sediments show a different pattern. Though these metals show high concentration levels in the turbidity maximum, the increasing trends continue in the downstream direction. The metal concentrations have been compared to effects range-median (ERM) guideline values (Long and others 1995) and average shale values (Turekian and Wedepohl

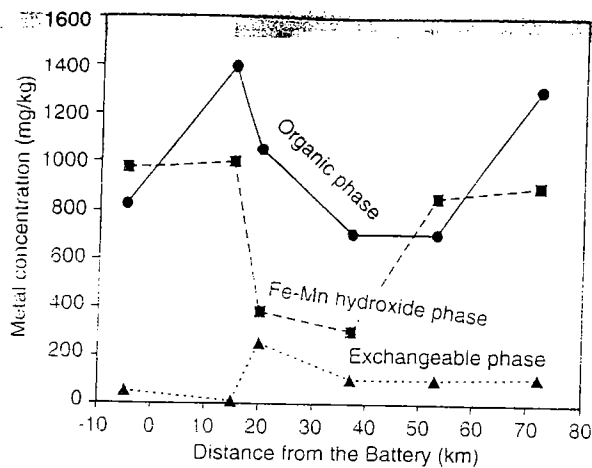


Fig. 5
Major geochemical transport phases for metals in the bottom sediments

1961) in order to emphasize the magnitude of metal enrichment (Table 1). The ERM values are the concentrations above which toxicity or other effects frequently occurred in toxicity studies by the National Oceanic and Atmospheric Administration (NOAA). The average shale (fossil argillaceous sediments) offers a comparison between pre-industrial and present-day metal concentration levels in the suspended sediments. The metals (Cu, Zn, Cd, and Pb) in the suspended sediments from the turbidity maximum are highly enriched in comparison to the ERM guidelines and average shale metal values. The most contaminating is Cd (maximum concentration in the turbidity maximum is 12 times the ERM values and 580 times the average shale values), and Cu (ERM, 7×;

shale, 42×) followed by Zn (ERM, 2.4×; shale, 10×) and Pb (ERM, 1.4×; shale, 16×).

Discussion

In Haverstraw Bay, the surface-water SSCs varied spatially less than the bottom concentration, though there are fluctuations between km 60 and 80. The 1991 sampling in the Hudson River estuary (Gibbs 1994) showed much less variation for the surface SSC. The highly fluctuating bottom SSC in this region of Haverstraw Bay can be due to channel bottom erosion. The erosion is possible because sill structures across the channel, between km 50 and 75, constrict flow and thus increase flow velocities (Cooper and others 1988). Also, abrupt decreases in channel depth and changes in cross-sectional area (Dronkers and van de Kreeke 1986) at many locations force intruding saltwater during flood tides to move upward into the downstream-flowing freshwater. The turbulence at the freshwater/saltwater interface results in fluctuating surface and bottom SSCs in this part of the Haverstraw Bay. The suspended sediments in the water column, especially the bottom waters in the turbidity maximum, consist of 50–60% fine mud (dominantly <2- μ m fraction). The sediment sorting of this nature and the high percentage of fines were not seen in upstream tributaries. The primary particle size distributions of the suspended sediments in the Mohawk River and the Upper Hudson are largely different from the suspended sediments in the turbidity maximum of Haverstraw Bay. There is an abrupt fining of sediment particles downstream of the Troy Dam, with noticeable increase of 11–26% in the clay size fraction. There is no known addition of fine particles into the

Table 1

Metal distribution (μ g/g) in the lower Hudson River estuary. The highest concentrations are compared with ERM toxicity guidelines (Long and others 1995) and average shale metal values (Turekian and Wedepohl 1961). na: not analyzed

distance from the Battery (km)		Cu (μ g/g)	Zn (μ g/g)	Cd (μ g/g)	Pb (μ g/g)
14		807	880	9	355
46		496	755	26	197
54		1890	462	116	216
59		978	647	19	62
70		NA	983	18	96
80		1040	NA	28	95
120		442	793	13	NA
Hudson River	ERM (μ g/g)	270	410	9.6	218
NOAA toxicity values (μ g/g)	maximum toxicity enrichment in the turbidity maximum	7	2.4	12	1.4
Average shale metal values (μ g/g)	pre-industrial metal values (μ g/g)	45	95	0.2	20
	maximum historical metal enrichment in the turbidity maximum	42	10	580	16

Table 2

Spearman's correlation coefficients, r , between metals and $<2\text{-}\mu\text{m}$ fraction of the suspended sediments and percentage of fine mud in the suspended sediments from Hudson River estuary ($n=8$). Significant correlation ($p < 0.005$) coefficients are in bold

	SSC	Fe	Mn	Pb	Cr	Ni	Cd	Zn	Cu	$<2\mu\text{m}$
$<2\mu\text{m}$	0.96	0.86	0.81	0.83	0.43	0.22	0.88	0.73	0.82	1.00
Mud	0.95	0.80	0.87	0.92	0.42	0.14	0.94	0.62	0.91	0.98

Haverstraw Bay other than by the Mohawk River and the Upper Hudson River; and other sources of fine particles, the input from shoreline erosion and in situ biological production, have been suggested as insignificant (Ellsworth 1986). The input from the shoreline is insignificant because it constitutes less than 1% of the fine load, and in situ biological production is considered insignificant due to its seasonal nature. The increase in fine sediments is probably caused by Troy Dam trapping coarse sediments and allowing fine particles to be carried downstream.

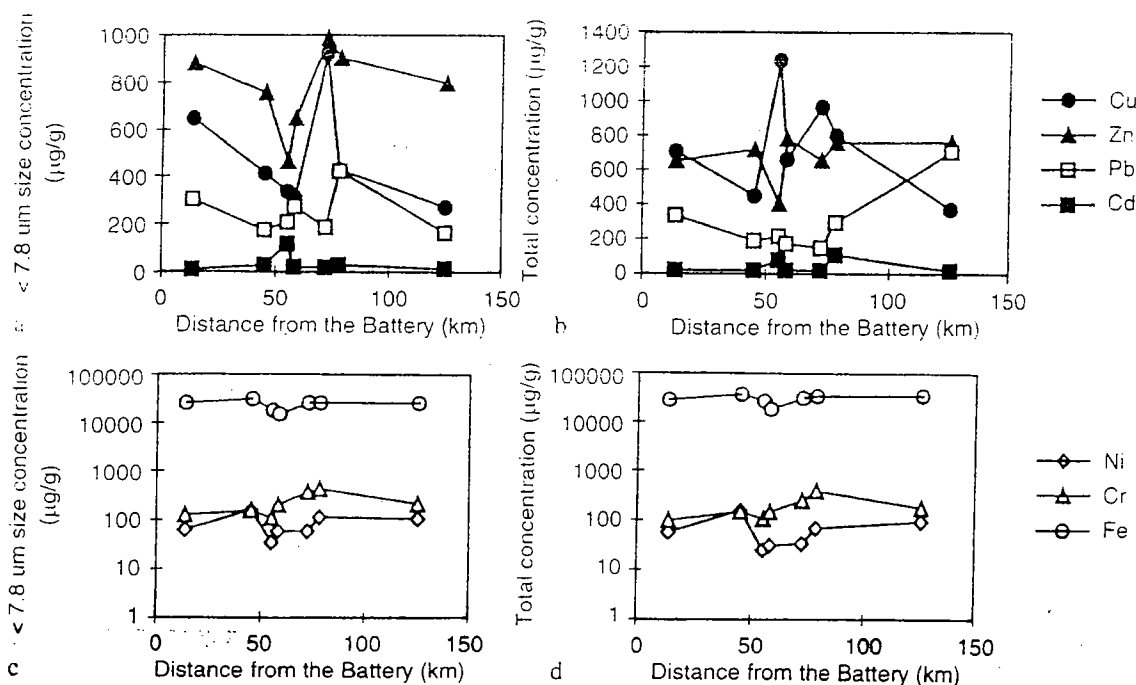
The accumulation of fine sediments has very high concentrations of heavy metals compared to upstream and downstream locations with the exception of Ni, Fe, and Mn. High correlation between metals and suspended clay particles explain the similarity in distribution patterns among metals (Table 2). The sediment metal concentrations were normalized with Al and Fe to correct for grain-size effects. Normalized and non-normalized metal concentrations do not show any changes in trends in the turbidity maximum of Haverstraw Bay due to the dominance of clay-sized particles in this region. Towards the harbor, there are significant variations in the distribution patterns among normalized and non-normalized metals, obviously due to the increase in coarser particles. In other

tide dominated estuaries the heavy metals show a remarkably uniform distribution when normalized to Fe or Al, which confirms the important inverse grain-size relationship (Coakley and others 1993; Grant and Middleton 1993).

Identifying the sources for high levels of metals in the Hudson River estuary is not an easy task. Particulate metal concentrations from the Upper Hudson and Mohawk Rivers are almost equal or in the same range as in 14 km from the Battery downstream (Fig. 6a, b). This observation does not necessarily prove that the tributaries are the only sources of metals in and around the Battery, New York, but indicates that they are important sources. The New York City Department of Environmental Protection (1987) found significant lowering of temporal and spatial metal levels, attributing this to the low input of metals from point sources. Thus non point sources contributing trace metals, routed through the tributaries (the Mohawk River and the Upper Hudson) account for the

Fig. 6a-d

a Accumulated metal concentrations in the $<7.8\text{-}\mu\text{m}$ fraction, b non-accumulated metals in $<7.8\text{-}\mu\text{m}$ fraction, c accumulated metals in $<63\text{-}\mu\text{m}$ fraction, d and non-accumulated metals in the $<63\text{-}\mu\text{m}$ fraction of the bottom suspended sediments



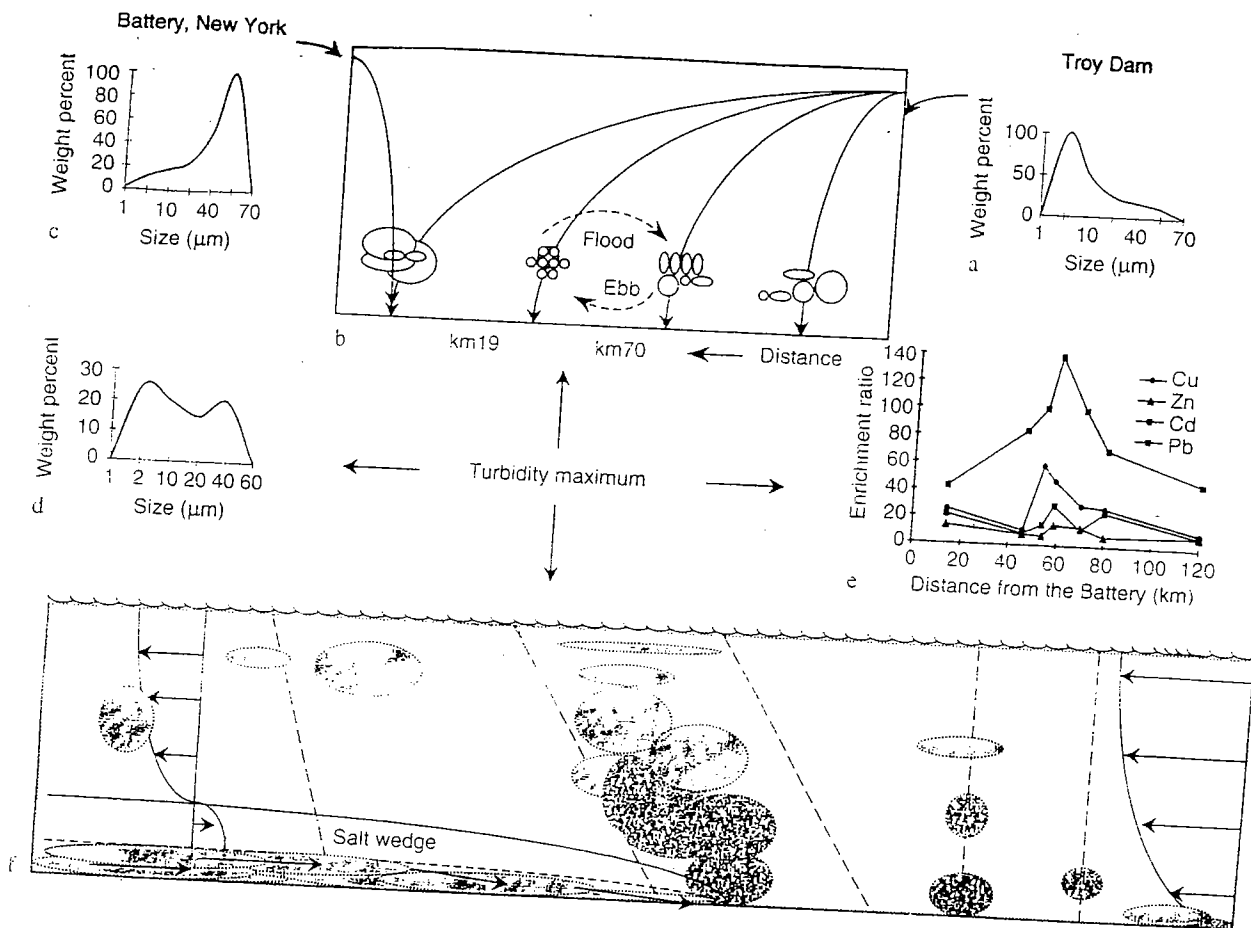


Fig. 7a-f

Schematic diagram showing possible dynamics of mud and metal accumulation in the Hudson River estuary turbidity maxima. a Particle-size distribution, the Troy Dam. b Model distribution, the Battery, New York. c Particle-size distribution, the Haverstraw Bay. d Particle-size distribution, the Haverstraw Bay. e Heavy metal accumulation in the Haverstraw Bay. f Model showing aggregation/disaggregation cycles in the turbidity maximum at the fresh/saltwater interface

may be carried downstream and deposited as aggregates in the George Washington Bridge turbidity maximum. The incoming floods carry them back to Haverstraw Bay.

Enriched metals like Cd, Cu, Pb, and Zn are well correlated with sediment surface area (Fig. 4b). In contrast, metals such as Cr, Al, Fe, and Mn are poorly correlated, suggesting no enrichment. These correlations are explained by the chemical fractionation study by Stamoulis and others (1996). They found that Fe-Mn hydroxide coatings and organic phases are the major carrier phases of metals in Hudson River estuary (Fig. 5). The metals such as Cd, Cu, Pb, and Zn are preferentially associated with Fe-Mn hydroxide, thus explaining correlation with surface area. Metals such as Cr, Al, Fe, and Mn are probably being shared by organic matter phase, which are particles with a wide range of sizes (Stamoulis and others 1996). Thus the enriched metals in the turbidity maximum are size-controlled and take part in deposition/suspension cycles.

Figure 7 is a conceptual model describing probable dynamics of the turbidity maximum in Haverstraw Bay and possible effects on fine-mud and size-controlled metal accumulation. Figure 7a shows the nature of sediments from Troy Dam. These finely skewed source sediments take part in the turbidity maximum cycles in Haverstraw Bay. Two-layer flow results in a turbidity maximum at the salt-freshwater interface (Fig. 7f). When fresh water

enriched metals to the Hudson River Estuary. Nonpoint sources consist of a multitude of pathways for trace metals, which include street runoff, seepage, groundwater infiltration, agricultural runoff, and snowmelt runoff. For example, Rohmann (1988) in his investigations estimated that nonpoint sources released 762 times more lead than point sources in the Hudson River. Thus it is likely that non-point sources are the main sources of metals in the turbidity maximum. High concentrations of Cd in soft tissues of Zebra mussels (Secor and others 1993) are indicative of large input of Cd in to the Hudson River estuary.

The entrapment and accumulation of fine sediments and metals in the turbidity maximum may have an increased residence time in Haverstraw Bay. This is likely because of the presence of the second turbidity maximum at km 19 (Bokuniewicz and Arnold 1984). The fine sediments resuspended in the Haverstraw Bay turbidity maxi-

with suspended load meets traces of saline water, small flocs (groups of dots) begin to form. Between km 46 and 80 in Haverstraw Bay the enhanced flow around sills results in increased suspension. The flocs disintegrate in the shear and fines are transported downstream or, during slack tide, preferentially reaggregated in the bottom layers. The incoming flood once again transports the aggregates back to Haverstraw Bay (Fig. 7b). Since the coarse sediments are trapped upstream, the aggregates in the turbidity maximum consist mainly of finer mud and enriched metals. Other studies of estuarine turbidity maxima demonstrated opposite effects, where there is a relative decrease in the proportion of fine particles and consequently in metal concentrations (Biggs and others 1983; Grant and Middleton 1993; Coakley and others 1993; Turner and others 1993). This is possible in such systems, since disaggregated and resuspended fine particles escape to the coastal ocean and/or the sediments mix with incoming uncontaminated coastal-derived sediments. In the Hudson River estuary, the disaggregated fine sediments most likely take part in aggregation and disaggregation cycles between the George Washington Bridge and the Haverstraw Bay turbidity maxima, and do not escape to the coastal waters immediately. Thus large amounts of fine mud and metals in the Haverstraw Bay turbidity maximum (Fig. 7d) probably result from a combination of processes such as the hydrodynamic sorting partly effected by the dam and the cycling of sediments between Haverstraw Bay and the downstream turbidity maxima. Similar enrichment of finer-size fractions and contaminants were also observed in Chesapeake Bay (Nicols and others 1982; Helz and Hugget 1987). Wolanski and Gibbs (1995) observed that silt and fine-sand dominating flocs of the Fly River are structurally weak and readily broken by increasing turbulence. The relatively fine particles in Haverstraw Bay may be contributing to the strength of the aggregates. The combination of these processes (sorting of sediments, strong aggregates, and transport of sediments between two turbidity maxima) may be responsible for the accumulation of the mud and associated metals. The higher levels of contaminants in the Haverstraw Bay and lower Hudson estuary sediments are a major concern since dredging and other human activities resuspend them in large quantities. The large-scale resuspension could change the bioavailability patterns of the contaminants associated with the sediments.

Conclusions

The fine mud and metals in the Haverstraw Bay turbidity maximum are most likely accumulated due to a combination of processes such as the fining of sediments effected by the dam at Troy and the cycle of sediment movement among two turbidity maxima. The abrupt decrease in channel depth and erosion of bottom provide the sediments in the Haverstraw Bay turbidity maximum. A bimodal particle-size distribution characterizes the up-

stream sediments, while the relative proportions of the coarser particles are much lower in the turbidity maximum. The accumulation of finer mud in the turbidity maximum results in the enrichment of metals. Cd, Pb, Cu, and Zn are enriched to high levels in comparison to average shale metal values and ERM guidelines. The enriched metals are strongly correlated with the particle surface area and are associated with Fe-Mn hydroxide coatings. It may be concluded that the Haverstraw Bay turbidity maximum acts as a temporary storage for fine mud and metals. The storage of mud and enrichment of metals seems to result from the aggregation/dissaggregation cycles and transport of sorted sediments between the turbidity maxima. Further studies are essential to understand and establish the relationship between the deposition/resuspension cycles between the two turbidity maxima and the residence time of the particles in the estuary.

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CLAYS OF HUDSON RIVER

CLAY MINERALOGY OF THE HUDSON RIVER AND ESTUARY

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ABSTRACT

Bottom and suspended sediment samples from along the lower 120 km of the Hudson River estuary, U.S.A., were analyzed for their clay mineralogy. A uniform composition along the estuary was found for mica ($65\% \pm 4$), chlorite ($24\% \pm 4$), and kaolinite ($10\% \pm 1$). Only smectite exhibited a trend by its absence in the upper estuary above 60 km and being $< 5\%$ in the lower estuary. This uniform clay mineralogy (CM) is attributed to the strong tidal currents mixing the flocs with uniform CM along the estuary.

INTRODUCTION

Background on Clay Minerals Trends

The lateral variations of the clay minerals (cm) in bottom sediments extending seaward from river mouth has been discussed by Van Andel and Postma (1954), Porrenga (1966), Powers (1957), and Edzwald and O'Melia (1975). The studies by Griffin and Ingram (1955), Powers (1954), and Nelson (1960) postulated that diagenetic processes caused the clay mineral trends that were

encountered in the coastal plain estuaries. Later, the work of Russell (1970) and Drever (1971) discounted the idea of diagenesis and showed that the clays were subjected to cation exchange reactions without changing the clay minerals themselves. Another potential source of clay mineral trends in an estuary or shelf is multiple inputs (ocean and river) of clay minerals was postulated by Postma (1967) and Meade (1972) as being caused by estuarine circulation which brought in different clay minerals landward from the ocean. This was followed by the work of Hathaway (1972) and Gibbs (1977) that suggested a primary particle size segregation with distance was causing a trend in the clay minerals on shelves. In addition, the process of differential coagulation was postulated as a mechanism causing trends in the clay mineralogy of bottom sediments of estuaries by Whitehouse et al. (1960), Edzwald and O'Melia (1975) and discussed by Gibbs (1977). The work of Allen (1991) on the Severn estuary showed fairly constant composition down the estuary and a dominant source of clays coming in from the river. The CM in the Fly River basin and delta was reviewed by Harris et al. (1993), but he didn't give detail CM trends. The work of Subramanian and Jha (1988) on the CM in the bed sediments of the Ganges showed no clear trends in the lower 125 km Hoogly River (part of the Ganges). In Europe the river/estuaries studies of Boldrin et al. (1988) on the Po and that of Gallene (1974) on the Loire are worth mentioning. In three estuaries in Georgia, U.S.A., Windom et al. (1971) found clay minerals coming in from both the ocean and rivers. An interesting study of 34 rivers around New Zealand (Churchman et al., 1988) showed mica dominated along with smectite.

Background on Hudson River Estuary

Intrusion of sea water varies between 50 and 110 km (35 and 75 miles) from the ocean, and its location is dominated by freshwater discharge and secondarily affected by tidal phases (Abood, 1974; Posamentier and Raymond, 1979). Stratification decreases downstream from furthest intrusion, but vertical circulation is relatively low above The Battery (Posamentier & Raymond, 1979), except near shallow margins where mixing reduces stratification. Tidal power is greatest below Haverstraw Bay and stronger during flood than ebb (Abood, 1974; Panuzio, 1963). Surface currents reach 2 m/s (NOAA, tide tables, 1992). Pritchard et al. (1962) and Jay and Bowman (1975) conducted additional investigations of the physical structure and circulation in the lower Hudson. The existence of two turbidity maxima is perhaps distinctive of the Hudson. One maximum in Haverstraw Bay is related to the salt/fresh water interface. A second maximum near the George Washington Bridge appears to be caused by lateral circulation induced by hydrodynamic constriction.

Aims

The purpose of this paper is to present the results of the clay mineralogy of the Hudson River estuary and lower Hudson River and to postulate the role of flocs in the transport and deposition of clay minerals.

METHODS

The samples for this study were collected near the center along the length of the Hudson Estuary/River up to 120km from the ocean (Figure 1). The samples were collected from the bottom of estuary using a pipe dredge that sampled the surface 8 cm, with the exception of two filtered samples of flocculated suspended material. The samples were deflocculated by dialysis to remove sea water, treated with sodium hexametaphosphate and size segregated by standard centrifugal techniques (Jackson, 1956) to obtain the less than 2 micrometer fractions. These muds were then mounted on glass slides using the smear technique to produce oriented clays (Gibbs, 1965). The analysis was conducted on a Phillips X-ray diffraction unit using $\text{CuK}\alpha$ radiation (35 Kv and 20 Ma) with Ni filter with a Phillips monochromator between $2-14^\circ 2\theta$ and $22-26^\circ 2\theta$ utilizing standard techniques (Gibbs, 1967) and the percentages determination followed the procedure of Biscaye (1965).

RESULTS

The trends of clay minerals up the estuary from the ocean are presented in Figure 2, and they show that the percent of mica, chlorite and kaolinite remains constant from the ocean to 120 km inland in the bottom sediments and that smectite is the only mineral (rather small in percentages, always less than 5%), that shows a minor trend from 0 to 60 km, whereas above 62 km from the ocean there is no smectite present in the bottom sediments.

DISCUSSION

These percentages of clay minerals are remarkably constant throughout the entire estuary of the Hudson River as well as 120 Km up the river. The sample at 120 Km from the ocean is in fresh water and would be before significant coagulation occurred. Most all of the other studies of estuaries, as discussed in the Introduction, showed some trends in the minerals changing along the length of the estuary. Allen's work (1991) in the Severn estuary showed similar results to this study, in having a nearly constant composition along the estuary. The Severn estuary, like the Hudson estuary, has high tidal currents.

In the case of the Hudson River, the input of suspended clay minerals comes in from the Hudson River. The clay minerals then coagulate forming flocs (coagulation observed by microscope) at about $\frac{1}{2}$ ppt salinity. This coagulation occurs upstream of the salt water intrusion so its position would shift with river discharge between 50 and 1150 Km from the ocean. Once formed it is postulated that these flocs are carried back and forth by the strong tidal currents, to produce this uniform composition. In Figure 3 the photomicrograph of the flocs in suspension shows all the clays in flocs with clear water between them. The only trend found is for smectite where a small amount (2-5%) in the lower 60 km of the Hudson estuary from New York Harbor up into lower Haverstraw Bay. This smectite percent correlated with the trend in the salinity due to intrusion from the ocean. The smectite could be imported from the ocean -- but still in all, it is a very low amount.

In suspended samples from 18 and 78 Km in from the ocean the composition of the CM in the flocs in suspension has the same composition as the bottom mud beneath it and is the same for flocs from widely different locations (not shown on graph). These observations suggest that coagulation "freezes" the composition of the flocs and then the flocs are distributed along the estuary.

In the case of the Hudson River, it appears that differential flocculation does not have an effect. If it did, a change in the percent of mica and kaolinite as it coagulates above Peekskill would be observed because based on the work of Whitehouse et al. (1960) and Gibbs (1983) it would be expected that these clays would coagulate first at a couple ppt salinity. It has been shown that illite alone coagulates 2½ times as fast as kaolinite alone at the salinity of the first coagulation (Whitehouse et al., 1960; Edzwald et al., 1974; Gibbs, 1983). The differential coagulation studies on clay minerals mostly studied individual clays not natural mixtures with coatings and what probably is occurring is a mutual coagulation of these natural mixtures. Likewise, the primary particle size segregation doesn't seem to be prevalent as was proposed by Gibbs (1977). Gibbs' (1977) study of the Amazon River showed trends in clay minerals over 1400 km, whereas this study is less than 120 km and the distance may simply not be large enough to produce this trend. The complete lack of a trend would indicate that the flocs once formed in upper Hudson River estuary are then just being distributed along the entire length of the estuary with no segregation of the minerals by primary particle size. Or else the mica, kaolinite and chlorite have the same primary particle size distributions and therefore could not be size segregated. Smectites are usually the smallest particles relative to the other clays and therefore would be the easiest to size segregate -- but the Hudson River supplies none. There

is a minor trend of smectites coming in from the ocean in the lower 60 km of the estuary. The work of Hathaway (1972) showed trace amounts of montmorillonite in these offshore areas, so the ocean would appear to be a significant source. There are, however, a number of other rivers and man-made sources which could cause this minor (<5%) trend.

This study shows that CM progressive change with distance in estuaries and off river mouths is not always to be expected. This has implications for (1) predicating sediment patterns of fine-grained sediments and (2) predicting sediment source in studies of ancient mud records. Just because no trend is found in ancient sediments does not rule out a estuary/river mouth environment. Since these clay minerals are the major toxic substance carriers in these environments, these findings are of interest to researchers involved in toxic transport and modelling. It should also indicate that coagulation as a mechanism controlling size and composition in geological and engineering studies should be studied and encouraged in future studies.

CONCLUSION

The Hudson River estuary exhibits a uniform clay mineral composition along the lower 120 km except for a minor (< 5%) amount of smectite toward the ocean. While many other estuaries show trends, in the case of the Hudson River estuary this lack of a trend is attributed to coagulated clays being homogenized along the estuary by high tidal currents.

FIGURE CAPTION

FIGURE 1. Area location map.

FIGURE 2. Clay mineral percent versus distance from ocean (km) for Chlorite (*), Kaolinite (□), Mica (+) and Smectite (■) in bottom sediments.

FIGURE 3. Photomicrograph of suspended floc from Hudson River Estuary. Bar is 100 μm long.

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