ORIGINAL ARTICLE

Mercury enrichments in core sediments in Hugli–Matla–Bidyadhari estuarine complex, north-eastern part of the Bay of Bengal and their ecotoxicological significance

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Abstract Mercury concentrations (Hg_T) in fine-grained fraction (<63 μm) of core sediments of the Hugli–Matla–Bidyadhari estuarine complex, India were analyzed. Results revealed a wide range of spatial variations (<4–93 ng g^{-1} dry weight) with a definite enhancement level at the lower stretch of the estuarine complex infested with mangrove plants, which might act as a sink to Hg_T. An elevated concentration of Hg was encountered in surface/subsurface layer of the core in majority of the cases resulting from physical, biogenic and postdepositional diagenetic processes that remobilized and resuspended the metal from deeper sediments. A strong positive correlation was observed between the Hg and clay fraction content of the sediments, while the correlations of Hg with Al, Fe and Mn were poor. Based on the index of geoaccumulation (I_{geo}) and effects range-low (ER-L) value, it is considered that the sediments are less polluted and thus there is less chance of ecotoxicological risk to organisms living in sediments.

Keywords Mercury · Sediment · Sediment quality test

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Introduction

Mercury (Hg) is one of the most toxic metals for marine fauna with a complex biogeochemical cycle in air, soil, water and biota. It is listed as a priority pollutant by international agencies in charge of marine environmental protection (Beiras et al. 2002; Ikem and Egiebor 2005; McAloon and Mason 2003). Mercury occurs naturally in the environment and can also be released from anthropogenic sources like antifouling paint for the hull of ships, slimicides used in the lumber and paper industries, pesticides, and seed dressings in agriculture and in pharmaceuticals. This metal is widely dispersed and has produced elevated mercury deposition rates around the world (Carreón-Martínez et al. 2002; Hylander 2001; Silva et al. 2003) including west and northwest Greenland (Riget et al. 2007). Most of the sources of mercury in aquatic ecosystems are from the atmosphere, primarily associated with rainfall. Atmospheric deposition contains the main three forms of mercury (Hg^{2+}, $Hg°$ or MeHg), although the majority is inorganic mercury (Beiras et al. 2002; Carreón-Martínez et al. 2002).

Once in surface water mercury enters in a complex cycle where one of its form can be converted to another. It can be brought to the sediments by particle settling and later released by diffusion or resuspension. Mercury can enter the food chain, or it can be released back to the atmosphere by volatilization (McAloon and Mason 2003; Marins et al. 1998). Mercury entered the environmental history because it was the first metal with a direct connection between concentrations in water, bioaccumulation in the food chain and a serious impact on human population (Jackson 1998). The Minamata disease, a worst outbreak of mercury pollution caused the death of many people who had eaten fish with high concentration of mercury discharged in water

and recycled by food chains. Cossa (1995) estimated that 5% of Hg discharged into the Mediterranean turns up again in the sea fish species rendering them unfit for human consumption. Mercury pollution not only constitutes a threat of life in the oceans but also the survival of humans if its prevention and control measures are not taken in proper time.

Elemental Hg and methylated Hg are neurotoxic, while inorganic mercury salts are nephrotoxic. Methylmercury (MeHg) is of particular importance, due to its ability to pass through biological membrane, its high chemical stability, and low elimination rates from organisms. This is the only mercury species that biomagnifies to a higher degree into the food chain (Carreón-Martínez et al. 2002; Ikem and Egiebor 2005; Hylander 2001).

The input of mercury in the littoral sediments and waters is variable in different parts of the world. According to an estimate presented by Barnabé and Barnabé-Quet 2002, the input of mercury to littoral areas of French River is 2.6–5.6 tones per year and concentration of mercury in molluscs vary from <0.2 tones >0.4 mg kg^{-1} of dry weight in relation to rearing zone. The Indian Sunderban (Latitude 21°32′ and 22°40′; Longitude 88°05′ and 89°E), as part of the vast delta (area 9630 sq km) at the mouth of the Ganges-Brahmaputra system is a unique bioclimatic zone in a typical geographical situation in the coastal regions of the Bay of Bengal. It has the potential for being a global biodiversity "hotspot" as it is a reservoir of very rich and diverse faunal and floral communities (Bhattacharya and Sarkar 2003). The estuarine stretch is the recipient of wastes from urban settlements and a variety of industries including paper and pulp, electrical, pharmaceutical etc. Hydrology of this estuarine system presents a cyclic pattern, characterized by a large amount of monsoonal precipitation and tidal interplay (Bhattacharya 1988; Sarkar et al. 1985). During the last few decades this coastal region is under the clutch of environmental degradation due to rapid human settlements, tourist activities, deforestation and increasing agricultural and aquacultural practices. A significant ecological change is pronounced in Hugli estuarine environment due to huge discharge of domestic, municipal and industrial wastes, dredged materials, storm water runoff, aerial fall out, oil spills, boating and other sources (Chatterjee et al. 2007) along with the rapid emergence of Haldia Port Complex, a major oil disembarkment terminal in eastern India (Sarkar et al. 2007). In addition to the untreated wastes from these "point sources", the estuary also receives the raw sewage sludge from 85 km upstream, discharge from highly urbanized metropolitan megacity of Calcutta (population 14.5 million) as well as the highly industrialized city of Howrah (Fig. 1). To date there are absolutely no data pertaining to Hg$_T$ composition of sediment profiles of this estuarine complex.

Hence the present collaborative study has been initiated to evaluate the geochemical factors that affect the spatial distribution of Hg$_T$ in the Hugli–Matla–Bidyadhari riverine complex of northeast India (Fig. 1).

Materials and methods

Study area

The Hugli–Matla–Bidyadhari estuarine complex of the lower deltaic plain of the Ganges–Bramhaputra delta covers a vast stretch of intertidal to supratidal mud deposits interlaced by numerous tidal creeks and intervening tidal shoals. From the Bay of Bengal face, the tidal range gradually decreases landward along the course of the estuaries and varies from semi-diurnal macrotidal to microtidal regime. The wind-driven wave climate is more pronounced at the mouth of the Hugli and Matla estuaries particularly during the monsoon months and is less significant in the Bidyadhari River lying in the upstream stretch of the Matla and Gosaba rivers. The hydrodynamic regimes decline from the west to east and from south to north in the estuarine complex. Tidal flushing throughout the year takes the primary role in sedimentation in the intertidal flats. These areas, however, suffer degradation and erosion under conditions of severe wave attacks during monsoon. Accordingly depending on variable salinity gradient, rate of flocculation and deflocculation together with suspension and resuspension processes have significant role in contributing the various thickness of sedimentary columns.

Ten sampling stations, namely Kakdwip (S_1), Lot No. 8 (S_2), Mayagoalinir Ghat (S_3), Jambu Island (S_4), Canning (S_5), Dhamakhali (S_6), Sandeshkhali (S_7), Diamond Harbour (S_8), Bajbaj (S_9) and Babughat (S_{10}), have been chosen considering the sediment dispersal patterns along the drainage network systems (Fig. 1) under typical tropical meso-macrotidal conditions. The studied stations belonging to different geomorphic and tidal environments have different wave energy fluxes and distances from the sea (Bay of Bengal) and have diverse human interference with a variable degree of exposure to heavy metal contamination. The study area can be divided into (1) Sunderban mangrove area, (2) non-mangrove areas of Sunderban and (3) upstream of the dominant Hugli River estuary adjacent to the megacity Calcutta and Howrah. Out of the total ten sampling sites, seven stations belong to Sunderban wetland. This wetland is infested with luxuriant mangrove vegetations and inhabited by many endangered species of flora and fauna representing genetically diverse ecosystems. Among those sampling sites, stations S_1, S_2 and S_3 are chosen from the Hugli River estuary in the

Fig. 1 Map showing the ten sampling locations
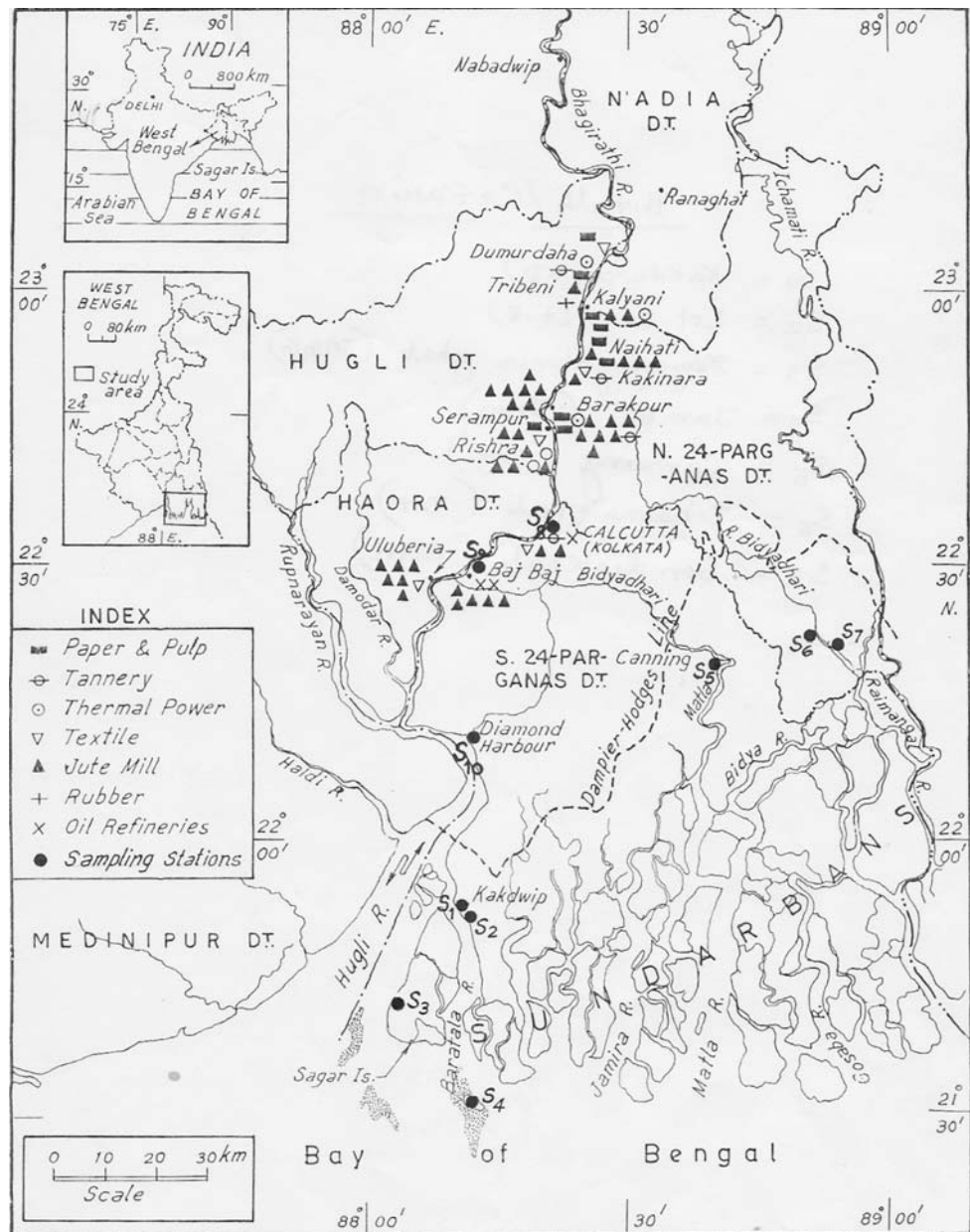
southwestern part of the study area, stations S_5, S_6 and S_7 from the Bidyadhari tidal river system and its complex network of tidal channels connected with the Matla River in the upstream part. Stations S_8, S_9 and S_{10} belong to the upstream part of highly industrialized stretch of the Hugli estuary in the northeastern portion of the study area. The station S_4, however, belongs to an offshore island at the mouth of the Hugli estuary having influence of dominant waves from the Bay of Bengal.

Sampling

During winter months (November–December 2005), cores of 30 cm length were collected with the help upto a steel corer (40 cm length and 5 cm diameter) by gently intruding it into the sediments and dug out, capped and frozen on return to the laboratory. The core length size differs between the stations due to variations in nature of the substratum. Each core sample was sliced into 4 cm fractions (sub samples) with the help of PVC spatula. Prior to sample collection, all the glasswares for the collection and storage of sediment samples were thoroughly cleaned with acid (10% HNO_3), and then rinsed in double-distilled water before each use.

Core fractions were stored in labeled polyethylene bags stored in iceboxes and transported to the laboratory where they were frozen to −20°C. Within 2 days, a portion of each sample was placed in a ventilated oven at a very mild

temperature (maximum 40°C) (Pereira et al. 1998). Dried samples were disaggregated and divided into two aliquots. One aliquot for measuring the sediment quality parameters (organic carbon, pH, % of silt, clay and sand) and the other part was sieved through 63 μm metallic sieves and stored in pre-cleaned, inert polythelene bags and stored at −20°C for elemental analyses. All the visible marine organisms and coarse shell fragments, sea grass leaves and roots when present were removed manually.

Analytical methods

In the laboratory organic carbon (C_{org}) content in sediment was determined following a rapid titration method (Walkey and Black 1934) and pH with the help of a deluxe pH meter (model no. 101E) using combination glass electrode manufactured by M.S. Electronics (India) Pvt. Ltd. Mechanical analyses of sediment were done by sieving in a Ro-Tap Shaker (Krumbein and Pettijohn 1938) manufactured by W.·S. Tyler Company, Cleveland, Ohio, and statistical computation of textural parameters was done by using formulae of Folk and Ward (1957).

Total determination of Al was performed by digestion of the sediments with a mixture of acids (HF, HNO_3 and HCl) according to the method described by Rantala and Loring (1975). Metal concentrations were determined by Flame-AAS (Perkin-Elmer Analyst 100) using direct aspiration into a N_2O–acetylene flame. Total mercury was determined by atomic absorption spectrometry using a silicon UV diode detector Leco AMA-254 after pyrolysis of each sample in a combustion tube at 750°C under an oxygen atmosphere and collection on a gold amalgamator (Costley et al. 2000). The accuracy of the methodology was ensured by frequent analysis of standard reference material for total Hg (estuarine sediment MESS-3) (designated concentration vs. observed concentration 0.09 ± 0.009 and 0.092 ± 0.002 μg g^{-1}, respectively). All the reagents used were of analytical grade or mercury free grade.

Results and discussion

Sediment characteristics

Sediment characteristics such as pH, organic carbon (%), and percentages of sand, silt and clay obtained in different profiles of the ten sampling stations have been shown in Table 1. Sediments are characterized by pH varying from slightly acidic to basic (6.6–8.8). The acidic nature mainly pronounced in Canning (S_5) is partly due to the oxidation of FeS_2 and FeS to SO_4^{2-} and partly results from the decomposition of mangrove litter and hydrolysis of tannin in mangrove plants releasing various kinds of organic acids (Liao 1990). Stations S_6 and S_7 even belonging to more mangrove infested areas have higher pH values because of the fact that pH is modified in these areas due to CO_2- carbonate system (Frontier and Pichod-Viale 1991). In addition, higher mean organic carbon values in S_6 and S_7 (0.78 and 0.94%, respectively) indicate the occurrence of more biogenous calcium carbonate and could possibly check the pH of the sediments from decreasing by the microbially-produced carbon dioxide through dissolution. This process of dissolution was also observed by Ghosh et al. (1992) in Sunderban mangrove environment. The sediment core samples show a variable admixture of sand, silt and clay with an overall size range from sandy to clayey very fine. The three stations (S_1, S_2 and S_3) morphologically belong to the intertidal mudflats of a macrotidal setting of the Hugli River estuary and showed a general homogeneity with dominant silty clay to clayey very fine material. The overall fine textural properties of the sediments in the core samples of the three stations indicate deposition from suspended and resuspended fine particles in a semidiurnal macrotidal regime. In a similar manner, core sediments of stations S_5, S_6 and S_7 showed suspensional finer deposits from the Matla–Bidyadhari tidal drainage complex in a macro-tidal setting with a dominant silty clay composition associated with a subordinate sand fraction (maximum of

Table 1 Sediment quality parameters of the ten sampling stations

Station	pH	Organic carbon (%)	Sand (%)	Silt (%)	Clay (%)	Texture
S_1	8.6 ± 0.17	0.52 ± 0.09	2.24 ± 0.51	41.97 ± 15.75	55.79 ± 15.73	Silty clay–clayey very fine
S_2	8.4 ± 0.21	0.74 ± 0.62	18.25 ± 7.26	47.42 ± 21.67	34.33 ± 17.84	Silty–clayey
S_3	8.5 ± 0.07	0.56 ± 0.02	3.15 ± 0.62	41.13 ± 11.67	55.71 ± 11.45	Silty clay–clayey very fine
S_4	8.1 ± 0.3	0.15 ± 0.16	99.74 ± 0.55	0.26 ± 0.55	–	Sandy
S_5	6.9 ± 0.2	0.73 ± 0.14	27.5 ± 6 .11	32.54 ± 11.19	39.95 ± 11.41	Fine loam–clayey fine
S_6	8.5 ± 0.16	0.78 ± 0.13	17.99 ± 5.21	37.58 ± 9.19	45.75 ± 9.62	Silty clay–clayey fine
S_7	7.9 ± 0.18	0.94 ± 0.12	10.05 ± 3.46	33.15 ± 9.74	56.79 ± 10.21	Silty clay–clayey very fine
S_8	7.9 ± 0.11	0.54 ± 0.05	0.54 ± 0.05	61.47 ± 19.8	37.69 ± 20.69	Silty–clayey very fine
S_9	7.8 ± 0.2	0.27 ± 0.18	0.27 ± 0.18	8.91 ± 5.46	–	Loamy sand–sandy
S_{10}	8.3 ± 0.3	0.51 ± 0.04	0.51 ± 0.04	63.11 ± 20.16	30.15 ± 20.18	Coarse silty–clayey fine

36.32%) compared to that of the former sampling stations (Table 1). The sand fractions in the sediments in these stations may be attributed to its mesotidal settings together with the higher influx of sand carried by flood tide from the mouth of the Matla systems. The absolute dominance of sand in the core sediments of Jambu Island (S_4) may be referred to its relatively high-energy intertidal beach setting influenced by wave and longshore currents.

Major elements in sediments

Core sediments from the Hugli estuary showed a wide range of Si/Al ratios (2.63–9.90) reflecting different mixtures of coarse and fine-grained materials (Windom et al. 1989; Din 1992). Organic carbon content also changed in a range of 0.09–1.87% suggesting the mixing of particles with different organic and lithogenic fractions. Concentration of Fe, Mn, Mg and Ca also revealed wide range of variations. Sediments of coastal environments are characterized (Table 1) by low organic carbon contents (0.06–1.87%). These values indicate a relative inorganic character of these sediments, which may have an important implication on the Hg geochemistry in the studied intertidal system.

Total mercury in sediments

The vertical distribution of total mercury (Hg_T) in different sediment cores at ten stations from Hugli–Matla–Bidyadhari tidal complex reveals low values as shown in Table 2 and Fig. 2. Low level of Hg_T was also recorded (0.08–0.294 μg g^{-1}) from upstream of Hugli estuary as well as in Sunderban mangrove wetland (Sarkar et al. 2004). The prevalent spatial variations in Hg_T concentrations in sediments are very much pronounced which might be governed by (1) wide variations of geographic–geomorphic situations, (2) natural variability associated with the physical mixing of the sediments, (3) differences in hydrodynamic regimes related to river discharge and tidal influx, (4) changes in sediment particle size characteristics (sandy to clayey very fine) and (5) non-homogenous inputs from point and non point sources of Hg. Levels of Hg_T ranged between <4 and 93 ng g^{-1} reaching its maximum value at Kakdwip (S_2) at 4–8 cm layer. Almost three-fold increase of Hg_T in the subsurface layer is encountered than the deeper layer (20–24 cm). Rest of the stations reveals almost uniform distributions in the sediment profiles. Based on the prevalent Hg_T concentrations, four distinct individual groups could be identified: (1)higher group comprising of four stations (S_1, S_2, S_3 and S_7) where Hg_T ranges from 15 to 93 ng g^{-1}, (2)moderate group comprising of three stations (S_8, S_9 and S_{10}) where Hg_T ranges from 14 to 24 ng g^{-1} and (3) lower group comprising of

Table 2 Concentration of total mercury (expressed in ng g^{-1}) in core sediment samples at ten sampling sites of Sunderban mangrove regions along with other elements

Sample no.	Hg_T (ng g^{-1})	Si (%)	Al (%)	Si/Al	Mg (%)	Fe (%)	Ca (%)
S_1/0–4	35	25.6	7.79	3.29	1.62	4.85	1.27
S_1/4–8	93	28.6	7.62	3.75	1.60	4.65	1.54
S_1/8–12	25	30.9	7.15	4.32	1.50	4.33	1.86
S_1/12–16	26	28.7	7.07	4.06	1.79	4.11	1.83
S_1/16–20	36	30.4	7.78	3.91	1.52	4.60	1.55
S_1/20–24	34	28.9	7.01	4.12	1.35	4.22	1.56
S_2/0–4	30	31.4	6.00	5.23	1.30	3.25	2.12
S_2/4–8	23	39.3	6.17	6.37	1.23	3.34	1.88
S_2/8–12	19	27.4	4.54	6.04	0.85	2.23	1.82
S_2/12–16	15	30.7	4.76	6.45	1.05	2.36	2.18
S_2/16–20	19	32.5	5.19	6.26	1.00	2.71	2.01
S_2/20–24	32	31.5	6.02	5.23	1.11	3.18	1.83
S_3/0–4	36	31.2	7.26	4.3	1.40	4.02	1.52
S_3/4–8	43	26.1	7.46	3.5	1.46	4.36	1.58
S_3/8–12	37	24.2	7.49	3.23	1.63	4.31	1.85
S_3/12–16	39	21.1	8.01	2.63	1.55	4.42	1.65
S_3/16–20	40	23.6	7.36	3.21	1.51	4.18	1.79
S_3/20–24	40	27.7	7.80	3.55	1.46	4.11	1.73
S_1/24–28	34	29.6	7.37	4.02	1.40	3.86	2.21
S_4/0–4	8	28.6	5.40	5.29	1.20	6.50	2.72
S_4/4–8	0.001	34.9	4.85	7.19	1.30	7.41	3.79
S_4/8–12	0.001	34.8	4.14	8.41	1.33	7.83	3.63
S_4/12–16	0.001	23.0	4.78	4.81	1.12	7.27	3.72
S_4/16–20	0.001	25.0	5.13	4.87	1.24	7.72	3.64
S_4/20–24	0.001	28.1	4.54	6.19	1.23	6.00	3.31
S_5/0–4	10	32.5	4.61	7.05	0.95	2.03	2.87
S_5/4–8	12	29.2	5.54	5.27	1.18	2.46	2.72
S_5/8–12	9	28.1	5.05	5.56	0.99	2.24	3.20
S_5/12–24	8	29.5	4.77	6.18	0.98	2.03	2.66
S_6/0–4	17	32.9	5.97	5.51	1.23	2.63	2.48
S_6/4–8	12	33.1	5.73	5.78	1.06	2.55	2.65
S_6/8–12	17	27.4	6.09	4.50	1.38	2.70	2.87
S_6/12–16	17	30.8	6.71	4.59	1.27	3.19	2.29
S_6/16–20	15	31.5	6.24	5.05	1.28	2.74	2.63
S_6/20–24	16	30.1	6.12	4.92	1.18	2.74	2.39
S_7/0–4	46	26.2	6.50	4.03	1.30	3.19	2.04
S_7/4–8	42	40.5	6.82	5.94	1.30	3.14	2.23
S_7/8–12	30	28.3	6.63	4.27	1.32	3.02	2.02
S_7/12–16	37	31.8	6.60	4.82	1.25	3.14	2.04
S_7/16–20	50	28.4	6.76	4.20	1.33	3.26	2.16
S_7/20–24	52	29.4	7.12	4.13	1.28	3.71	1.80
S_7/24–28	49	28.3	8.22	3.44	1.59	4.54	1.69
S_8/0–4	20	41	6.2	6.6	1.21	3.3	1.7
S_8/4–8	20	41	6.1	6.7	1.23	3.3	1.8
S_8/8–12	17	42	5.8	7.2	1.16	3.0	1.9
S_8/12–16	18	42	5.7	7.3	1.17	3.2	1.8

Table 2 continued

Sample no.	Hg_T (ng g^{-1})	Si (%)	Al (%)	Si/Al	Mg (%)	Fe (%)	Ca (%)
S_8/16–20	14	44	5.7	7.8	1.09	2.9	1.8
S_8/20–24	16	44	5.8	7.6	1.05	2.7	1.7
S_8/24–28	18	45	5.7	7.9	1.01	2.7	1.8
S_9/0–4	24	45	6.3	7.2	1.18	3.2	1.7
S_9/4–8	18	47	5.2	8.9	1.08	2.8	1.9
S_9/8–12	20	46	4.9	9.2	1.10	2.9	2.0
S_9/12–16	16	48	4.6	10	1.08	2.8	2.1
S_9/16–20	21	47	5.5	8.5	1.14	2.8	2.2
S_9/20–24	19	33	5.5	6.0	1.17	3.0	1.9
S_9/24–28	23	39	5.6	6.9	1.18	3.3	1.9
S_{10}/0–4	20	43	5.4	7.9	1.04	2.7	1.9
S_{10}/4–8	19	44	4.9	8.8	0.97	2.2	1.9
S_{10}/8–12	18	41	4.8	8.5	1.00	2.5	1.9
S_{10}/12–16	15	46	4.7	9.9	0.97	2.5	1.9
S_{10}/16–20	22	45	5.0	9.1	0.98	2.6	2.0
S_{10}/20–24	22	47	5.3	8.8	0.93	2.5	1.9
S_{10}/24–28	22	47	5.3	8.9	0.98	2.6	2.0
S_{10}/28–32	19	45	5.4	8.3	1.01	2.6	1.9
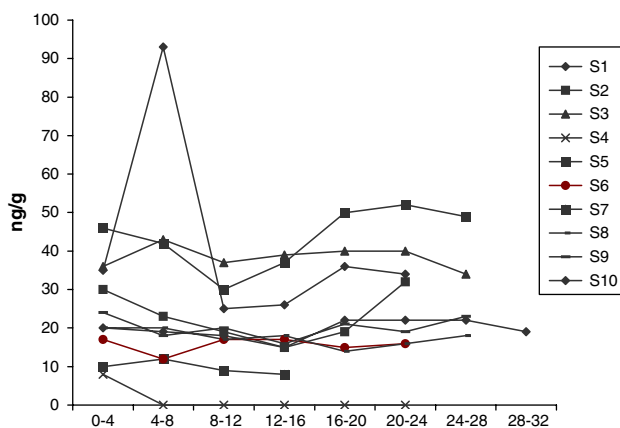
Fig. 2 Spatial patterns of total mercury (Hg_T, in ng/g) distribution in core sediment samples in ten sampling stations of Sunderban

two stations (S_5 and S_6) where, Hg_T is reasonably low than the first group (8–17 ng g^{-1}) and (4) almost pristine site formed by a solitary station (S_4) where Hg_T is about 12 times lower than the former stations in surface/subsurface layers. The station S_4 represents the lowest enrichment of Hg_T which may be attributed to minimal anthropogenic stresses and longest distance from the industrial belts of the city of Kolkata and Howrah located upstream of the Hugli estuary (Fig. 1). The highest values of Hg_T at three stations (S_1, S_2 and S_3) are attributed to the huge discharge of sediments related to flash flood from the upstream part of the dominant Hugli estuary during the four monsoon

months (July–October) (Goodbred 2003; Ram et al. 2003). A bulk of these sediments together with high T_{Hg} concentrations are suspended and recycled by the scouring effects of the dominant flood and ebb tidal currents in the lower stretch of the estuary during the postmonsoon season when the samples were collected. The phenomenon of sediment recycling and mixing is further aided by the dredging in the lower stretch of the Hugli River as well as biogenic activities of the macrozoobenthic animals (Bhattacharya 2002). The higher values of Hg_T at station S_7 is not very clear but might be related to the huge practice of burning of wood, charcoal and to some extent coal for preparing molasses and husking rice by the local inhabitants especially during winter months (January and February when the sampling was done). This results in the dispersion of Hg in a local scale (Mitra 1986). Moreover, high turbidity of the Bidya River throughout the year helps considerable retention of Hg within the estuarine system (Elliot and Griffiths 1986).

It is worthwhile to mention that three stations (S_1, S_2 and S_3) along the northeast and southwest stretch of Sagar Island (at the mouth of the Hugli estuary) are exposed to anthropogenic pressure primarily caused by high riverine traffic. The lack of standard norms and strict regulation about fuel being used in mechanized boats for ferrying and fishing throughout the year may lead to deposition of Hg at local scale. Moreover, a few patches of old mangroves (*Avicennia alba*, *A. marina*, *Rhizophora* sp and *Excoecaria agallocha* in these areas may have a role in accumulating Hg_T as pointed out by Lacerda et al. (2001) In addition, dental amalgam, batteries, thermometer, electric switches manufacturing industries located in the upstream of the Hugli estuary together with extensive use of antifouling paints by the coastal people act as potential sources of Hg.

Except sites S_1 and S_7 there is an increasing trend of total mercury enrichment at the surface/subsurface layer. This may be the result of postdepositional diagenetic processes that remobilize the metals from deeper sediments and cause upward migration in the sediment column. Rasmunssen (1994) and Canario et al. (2003, 2005) also found high Hg_T in surface sediments of the Tagus estuary, Portugal and interpreted that Hg may be mobilized under sub-oxic conditions and retained in the upper sediment layers mainly associated with Fe/Mn oxy-hydroxydes, where interactions strength of the binding between Hg and sedimentary phases also plays an important role (Silva et al. 2003). Mercury is also associated with the formation of strong aqueous complexes with dissolved sulfides like polysulfide and thiols. The formation of these compounds can be an important mechanism in the mobilization of mercury from reducing sediments to the water column (Bothner et al. 1980; Wang and Driscoll 1995). Other factors like the bioturbational activities of benthic

macrozoobenthos [*Sesarma* sp (crab), *Ocypode* sp, (crab), *Lumbrinereis notocirata* and *Mastobranchus indicus* (polychaetes)] present in the mudflat of Sunderban produce physicochemical changes (Bhattacharya 2002) that may contribute to the mobilization of Hg from the bottom to the superficial sediments and to the water column (Birkett et al. 2002). Transport, burial and diagenesis play a key role in the preservation of historical records for metal contamination (Valette-Silver 1993). Hence for reliable results, an excellent knowledge on the environment of deposition is urgently needed and the problem specific to each site is to be taken into consideration.

Detrital and authigenic Fe–Mn oxi-hydroxides, which accumulate in oxic sediment layers, can also be important scavengers of Hg (Jenne 1968; Farrah and Pickering 1978; Canario et al. 2003). The correlation between the distributions of iron and manganese with the total Hg in the surface sediments (between Fe and Mn $r = 0.871$, $p = 0.011$, Fe and Hg $r = -0.096$, $p = 0.839$) illustrates the probable importance of this scavenging process.

Sediment quality tests

ERL and ERM values

When mercury concentrations of the present study were compared to the effects range low (ERL) sediment toxicity value (0.15 µg g^{-1}) as reported by Long and Morgan (1991), it is revealed that all the sites are lower than ERL. However, these values are lower than those previously reported from the same estuarine environments (Sarkar et al. 2004).

Index of geoaccumulation (I_{geo})

Possible sediment enrichment of metals was evaluated in terms of the I_{geo} of Muller (1979). The formula used for the calculation of I_{geo} is: $\log_2 (Cn/1.5 Bn)$, where Cn is the measured content of element "n", and Bn the element's content in "average shale" (Turkian and Wedephol 1961). The geoaccumulation Index (I_{geo}) in the present work showed very low values (ranges from -8.817 at S_4 to -3.780 at S_7) indicating that sediments are uncontaminated (Muller 1979), endorsing previous observation reported by (Chatterjee et al. 2007) from the core sediment samples in Sunderban environment.

Enrichment factor values

Differentiating the elements originating from human activities and those from natural weathering is an essential part of geochemical studies. One such technique largely applied is "normalization" where metal concentrations were normalized to a textural or compositional characteristic of sediments. Normalizing elements relative to Al is widely used to compensate for variations in both grain size and composition, since it represents the quantity of aluminosilicates, which is the predominant carrier phase for adsorbed elements in coastal sediments. According to Nolting et al. (1999), this method is also a powerful tool for the regional comparison of trace metal content in sediments and can also be applied to determine enrichment factors (EFs).

The values of EFs can be obtained using the equation EF = (metal/Al) sediment/(metal/Al) shale. EFs close to unity point indicate crustal origin while those greater than ten are considered to be non-crustal source (Nolting et al. 1999). The minimum EFs obtained for mercury (0.052 at S_6–0.391 at S_5) in the ten studied stations are less than unity implying that this metal is depleted in some of the phases relative to crustal abundance in the study area. However, it is evident that majority of the other studied elements with a mean EF value greater than unity reveal sediment contamination, for example, the higher mean EF values for Mg, Fe, Ca and Mn. Overall higher EF values for Mg and Ca (except for S_1 and S_3) suggest the presence of enriched sediments derived from multifarious sources like domestic sewage, power plant discharges, etc.
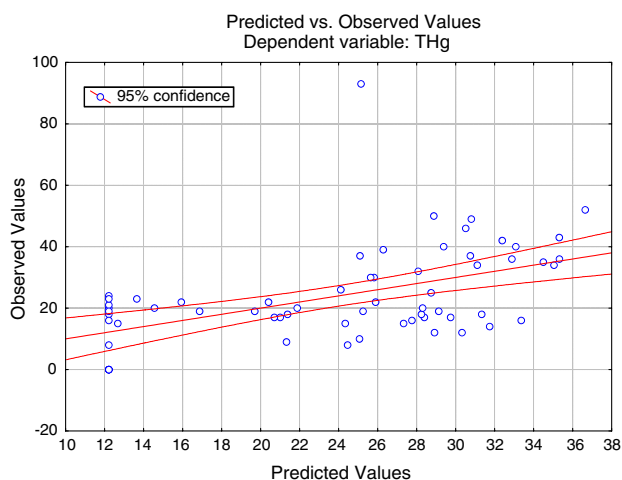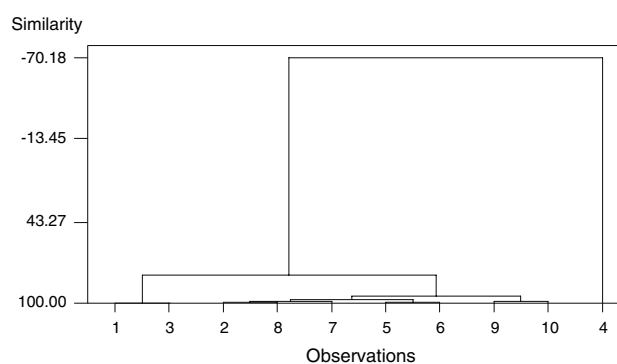
Statistical analyses

To establish the variation of the total mercury in ten stations, analysis of variance (ANOVA) was undertaken using mercury concentration as variables and stations and depth profiles as different factors. Significant value was obtained only for stations ($F = 15.73$; $p < 0.001$) but insignificant for depth profiles ($F = 0.34$, $p < 0.93$). Correlation values (r) between Hg_T and organic carbon, Al, Fe and Mn are shown in Table 3 which reveal an overall insignificant picture in majority of the cases. Birkett et al. (2002) indicated that organic matter is not a major factor that controls the mercury distribution, other factors like macroinvertebrates might be important. In aquatic systems the macroinvertebrates like mussels, cockles, polychaetes, and sea anemones present in the mudflat of estuarine environment may produce physicochemical changes that may contribute to the mobilization of mercury from the bottom to the superficial sediment and to the water column (Birkett et al. 2002). In sediment of oyster areas in Sonora, Mexico, similar non-significant correlations between exchangeable mercury concentration and Fe, Mn and organic matter, have been observed by Garcia-Rico et al. 2006. The lack of correlation between Hg:Fe, Hg:organic carbon, Hg:Mn and to some extent Hg:Al suggests other associated factors (e.g., bioturbation, tidal flushing, temperature variation). A strong positive correlation between Hg and clay fraction of sediments was found ($r = 0.51$; $p < 0.0001$, $n = 64$)

Table 3 Correlation coefficient (*r*) and level of significance (*P*) of Hg:C, Hg:Al, Hg:Fe and Hg:Mn in core sediment samples of Hugli estuary

Station	Hg:OC (%)		Hg:Al (%)		Hg:Fe (%)		Hg:Mn (%)	
	r	*p*	*r*	*p*	*r*	*p*	*r*	*p*
1	0.322	0.534	0.402	0.429	0.434	0.390	−0.055	0.918
2	0.440	0.383	0.804	0.054	0.789	0.062	0.094	0.860
3	0.275	0.550	0.316	0.489	0.688	0.087	0.523	0.228
4	0.993	0.000	0.0658	0.155	−0.422	0.405	−0.765	0.077
5	0.656	0.344	0.710	0.290	0.770	0.230	0.674	0.326
6	−0.140	0.791	0.590	0.218	0.499	0.314	0.809	0.051
7	0.531	0.220	0.454	0.306	0.572	0.179	0.325	0.477
8	−0.054	0.909	0.738	0.058	0.667	0.102	0.365	0.421
9	0.184	0.693	0.854	0.014	0.790	0.034	0.399	0.375
10	−0.252	0.547	0.640	0.087	0.265	0.526	0.176	0.677

which was observed in other estuarine environments (Panda et al. 1999; Sahu et al. 1998; Panda 1993). Clay particles have relatively high metal content due to greater active surface area and this favors to associate with finer grain particles (e.g., Cundy et al. 1997). Regression line (predicted vs. observed) of Hg_T with clay% is shown in Fig. 3. The broken lines represent the 95% confidence interval for all the data. There is a good fit between Hg_T and clay% i.e., a good linear relationship can be shown. The graph shows that the individual points lay within the 95% confidence level excepting few cases. In contrast, strong negative correlation was found for sand with Hg_T ($r = -0.49$; $p < 0.0001$; $n = 64$) reflecting these coarse fractions as a "dilutor" of the metal in sediments. Strong positive relation between total Hg and fine fraction of the sediment was also established by Ramalhosa et al. (2006).

A cluster analysis was carried out to identify any analogous behavior patterns of Hg along with Fe, Mn, Mg,

Fig. 4 Dendogram showing the relationship between sediment samples in terms of Hg_T, Si, Al, Cal, Mg and Fe in ten sampling Sites

Si and Al of the ten sampling cores, as shown in Fig. 4, which could be grouped into two clusters. The Euclidean distance of the standardized data was chosen as dissimilarity measurement. Cluster 2, comprising of the individual station 4 (Jambu Island) forms a clearly differentiated group of less polluted site. The rest nine stations, on the other hand form the first cluster, with subgrouping between individual stations with each other. The grouping was noticed between 1–3, 2–7–8, 5–6 and 9–10 depending on their differential exposures to differential levels of anthropogenic stresses.

Conclusion

The results obtained in this study indicate that sediment profiles in this tropical estuarine complex are less contaminated by mercury mostly related with distance to the industrial source, erosion, atmospheric deposition, combustion of fossil fuel, and with tidal dynamics. Surface–subsurface sediments showed elevated Hg_T concentrations when compared with deeper layers, reflecting the existence

Fig. 3 Regression line for correlation of total Hg with clay%. The *broken lines* represent the 95% confidence interval for all the data

of higher discharges of mercury in the recent years. The incorporation of anthropogenic mercury in sediments is not a simple function of distance from the source but depends on sediment characteristics. Vertical profiles of mercury distribution also indicate remobilization of mercury in reducing environments. Sedimentary processes, such as postdeposition migration and diagenesis, bioturbation activities and natural variability among the sites, make it unwise to conclude too much for the present observation and need continuous monitoring considering other polluted sites of interest in this vibrant environment.

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