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Prevalence and Ecotoxicological significance of heavy metals in sediments of lower stretches of the Hooghly estuary, India

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Abstract

The concentration and distribution of selected eight heavy metals in five stations from lower stretches of the Hooghly estuary were studied to ascertain the level of anthropogenic contaminant loading resulting from the development of the region. Atomic absorption spectroscopy showed that the mean concentration of Fe, Zn, Cu, Ni, Pb, Cr, Cd and As (mg kg^{-1}, dry weight,) ranged from 29950.70 – 39567.94, 61.45 – 98.83, 40.65 – 54.46, 25.44 – 42.78, 36.93 – 48.56, 29.07 – 46.35, BDL – 3.48 and 1.18 – 6.44 respectively. Pollution load index (PLI) and Index of geoaccumulation (I_{geo}) revealed overall low values but the enrichment factors (EFs) for Cd was typically high for three of the stations. Calculations based on Effect Range Low (ERL) and Threshold Effect Level (TEL) showed that the mean concentration of Cu, Ni and Cd and to some extent Pb exceeded these levels, indicating that there is chance of ecotoxicological effects on benthic organisms dwelling in this region. Inter-elemental relationship and cluster analysis revealed identical behavior of the elements during transport and distribution. The study will help to further the cause of environmental protection of this sensitive biorealm in conjunction with the need for development of the region.

Keywords: Ecotoxicology, Enrichment factor, heavy metals, Hooghly estuary, sediment.

Introduction

Mangroves are woody plants found in the tropical and subtropical latitudes which provide various ecosystem goods and services, viz. protection against cyclones, storms and coastal erosion, waste water purification, habitat for a wide range of wild flora and fauna, nursery ground for a variety of fishes and are a source of wax, honey, timber and medicine. Unplanned human development and globalization, has however, put them at peril. Numerous sources of pollution coupled with climate change have rendered these ecosystems vulnerable, such that they have become a subject of numerous studies on the effect of pollution. Of prime concern, recently, has been the effect of heavy metals on these estuarine systems. Heavy metals have been a cause of alarm because of their persistence, non-alterability and toxicity (MacFarlane & Burchett, 2000). Their input in various ecosystems has been a direct fall-out of mining and smelting, industrial activity, disposal of sewage sludge, agricultural and aqua-cultural practices and urbanization (Abdullah et al., 1999; Dragun et al., 2009; Shazili et al., 2006). Concerns arising out of multifarious developmental activities are the regular built-up of heavy metals to toxic levels in the aquatic environments, which find their way to the estuaries and finally to the oceans. It is because of their physico-chemical as well as biological properties that mangrove ecosystems tend to act both as sink and source of heavy metals (Evans et al., 2003; Harbison, 1986; Pekey, 2006; Rainey et al., 2003). Mangrove estuarine sediments, being anoxic, reduced, rich in sulphide and being high in organic matter and clay content, promotes the retention of heavy metals (Silva et al., 1990; Tam and Wong, 2000 in association with the mangrove flora that typically characterize such ecosystems. Hence, sediment is always regarded as the potential reservoir for metals and plays an important role in adsorption of dissolved heavy metals (Praveena, 2010; Wang & Chen, 2000). Elevated levels of heavy metals in sediments can be a reflection of diagenetic processes (Zwolsman, 1993) or grain size effects (Loring & Rantala, 1992) and may not be necessarily due to anthropogenic loading. Since it is difficult to separate the fractions of heavy metals coming from different sources, it is all the more vital to establish the expected natural background concentration level so that sediment quality indexes can be used to quantify anthropogenic inputs.

Metal ions are an essential requirement in physiology and metabolism, which become toxic when they exceed standard permissible limit (Salomons & Forstner, 1984). For example, Iron (Fe), Copper (Cu), Zinc (Zn), Nickel (Ni), Manganese (Mn) and Cobalt (Co) are essential micronutrients which exert toxic effects at concentrations exceeding the permissible limits. In contrast, certain metals like Lead (Pb), Cadmium (Cd), Chromium (Cr), Arsenic (As) and Mercury (Hg) are toxic even at very low concentrations (WHO, 2004). They are global contaminants and have been listed as the most hazardous inorganic contaminants on the US EPA Hazardous substance Priority List, having a detrimental effect on the health of people and ecology. These metals, when incorporated into the food chain, are biomagnified and pose a potential risk to human health (WHO, 2004; Alkarkhi et al., 2009).

Numerous investigations have been conducted to assess and establish the extent of metal contamination in mangrove sediments (Praveena, 2010; Attri et al., 2009; Shriadh, 1999). Most of these studies were focused on the total metal content in sediments, organisms and water bodies in order to have a better understanding about the health of mangrove ecosystem and ecotoxicological potential of heavy metals.

Our present study is designed at evaluating the distribution, enrichment and accumulation of heavy metals in sediments of the Sunderban estuarine region, India, in order to infer the possible influence of anthropogenic activities on the region. In the present study, we carried out characterization of the mangrove sediment, namely sand, silt, clay, total organic carbon (TOC) and the distribution of heavy metals such as Fe, Cu, Zn, Ni, Pb, Cd, Cr and As in five spatially separated stations along the Hooghly estuarine region.

The aim of the study is to assess the status of contamination of the sediments by (1) comparing with sediment quality guidelines (SQGs) by US EPA, (2) computation of pollution indices viz Enrichment factor, Geo-accumulation index (I_{geo}) and Pollution Load Index (PLI); and (3) evaluating the ecotoxicological significance based on application of two sets of guidelines: ERL/ERM and TEL/PEL and mean toxic units (Essien et al., 2009; Aloupi & Angelidis, 2001; MacDonald et al., 2000; Reddy et al., 2004; Selvaraj et al., 2004; Tomllinson et al., 1980; Woitke et al., 2003). Inter-elemental relationship and cluster analysis was used to identify the major factors influencing the distribution of heavy metals in the study area.

It is believed that using these Environmental quality indicators and indices to evaluate sediment quality and the effects on organisms therein would serve as a powerful tool for decision makers, managers, technicians and the public for processing, analyzing and conveying environmental information so that necessary interventions can be made in time to prevent the occurrence or aggravation of deleterious effects. This would further the cause of environmental conservation and protection of such ecosystems by embracing better management practices and adoption of ameliorative steps, where required.

Materials and Methods

Study area

The study area (Fig.1) in the Hooghly estuary (88°00´ - 89°28´E and 21°00´- 22°30´N) comprises of three coastal sites and two inshore sites in the Sunderban region of the Hooghly-Brahmaputra estuarine system in India. Sunderbans, a UNESCO World Heritage Site, is the world's largest prograding delta formed by the rivers Ganga , Brahmaputra and Meghna.

Innumerable tributaries of these three rivers crisscross the fifty four tiny islands which make up the world's largest estuarine forest. Sunderbans is spread in an area of about 9630 sq. km in the district of South 24 Parganas in West Bengal. The climate is mostly tropical. With average rainfall of approximately 1763 mm per year, the temperature varies from 20˚C, during December - January, to 28˚C during June – July. Humidity ranges between 70% to 80%. Sunderbans is densely populated and majority of the population depends on agriculture supported by other occupation like fishery, forestry and handicrafts. This watershed region has been an arena of intense ecological change due to growth of industries in the upstream region coupled with increase in human population. The direct fallout of the same has been huge discharge of domestic and industrial waste and an intensification of anthropogenic pressure resulting in vulnerability to chemical pollutants such as heavy metals, pesticides, chlorinated hydrocarbons etc. which would have an adverse impact on the quality of the local coastal environment (Saha et al., 2006; Sarkar et al., 2004; Sarkar et al., 2003; Sarkar et al., 2002). Abbas and Subramanian, 1984 calculated that at Kolkata (former Calcutta), the Ganges annually supplies 411×10^6 t (i.e., 328×10^6 t sediment + 83×10^6 t solute load) of total load to the Hooghly estuary.

The main sources of heavy metals in the Indian sunderbans are industries in the upper catchment area, fishing harbours, agricultural activities, Haldia sea port and disposal of urban wastes and sewage along the bank of the Hooghly estuary (Mitra, 1998).

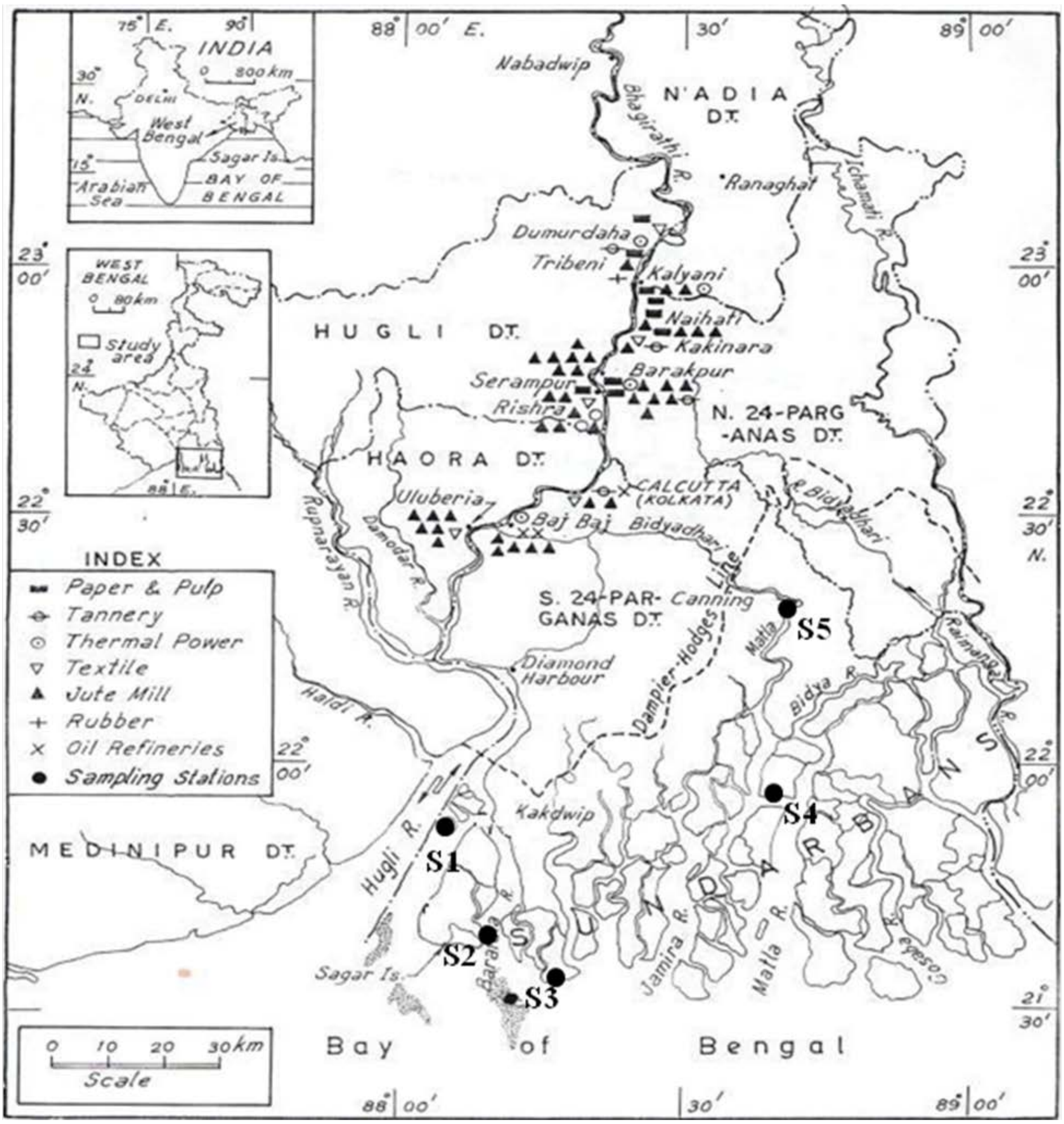

Fig.1. Map of Sunderban showing the location of the sampling sites (S1–S5) in Hooghly estuary.

Description of study sites

Five sampling sites, namely, Nayachar (S1), Chemaguri (S2), Henry's island (S3), Jharkhali (S4) and Canning (S5) were chosen in Sunderban wetland because they belong to different tidal environments, are at a varying distances from the sea (Bay of Bengal), have diverse human interference and are exposed to varying levels and sources of pollution (Fig. 1).

Nayachar is an island located at the confluence of Hooghly and Haldi River. It is at about 4 km boat ride from Haldia, a major seaport and industrial belt. Consequently, the island is exposed to pollutants from the industrial houses operating at Haldia. Besides, dredging operations to free Haldia port of sediments has resulted in increased energy fluxes in the region.

Chemaguri is a macrotidal creek located in the western part of Indian Sunderban facing the Muriganga River. The site is dotted with shrimp farms. Located on the western edge of the Sunderban, Henry's island, in Bakkhali, offers an interesting mix of beach and mangrove forest. Due to spurt in tourism in the area, the fisheries department of West Bengal has set up some lodges and a pisciculture project here, where breeding and cultivation of prawns and fishes are done.

Jharkhali village is surrounded by Herobhanga Reserve forest in the south and overviews the confluence of Baidya and Herobhanga rivers. People in Jharkhali colony practice agriculture during the monsoon season and are engaged in fishing for rest of the time.

Canning is situated on the south bank of the Matla River. It happens to be a major fish landing site and nodal point of entry to the Indian Sunderbans. Consequently it supplies and receives various articles of use to and from the Sunderbans. Land Use mostly comprises of agriculture and pisciculture. Besides, many are engaged in ferrying goods and people across the River Matla.

Sampling

Surface sediment from the five sampling stations was collected using a grab sampler during low tide. Triplicate samples were obtained at each site (Popek, 2003; Radojevic, 1999). All samples were labeled and stored in cool box with ice-pack at 4°C and transported to the laboratory at the earliest for further analysis.

Sediment digestion and analysis

In the laboratory, the sediment samples were oven dried at 70°C-80° C for 48 hours, gently ground with rolling pin to disaggregate the samples without altering the grain size of the sediments. Sediment component analysis was performed using the sieving technique according to Folk et al., 1957. Total Organic Carbon (TOC) was estimated using chromic acid digestion followed by back-titration with ferrous ammonium sulphate (Walkley & Black, 1934). The sediment samples were digested following procedure of Wang et al., 2010 using concentrated HNO_3 and $HClO_4$ (AR Grade). Prior to sample digestion all glass goods were washed with double distilled water, soaked overnight in 5% HNO_3, rinsed with deionized water and then dried in the oven. The determination of heavy metals was done by Atomic Absorption Spectrometer (Perkin Elmer Analyst 400). Mean values of three replicates of each sample was calculated and considered**.**

Quality assurance

Precision and accuracy of analysis were ensured through standard reference material from National Institute of Standards and Technology, USA (SRM 1646a: Estuarine sediment) with same digestion method and analytical procedure. Comparison of measured heavy metals concentration with certified values (mg kg^{-1} dry wt.) of the Standard Reference Material (1646a) was found to be in good consonance with recoveries ranging from 87% to 99% (Fe= 87%; Zn = 97%; Cu = 89%; Pb = 99%; Cd =91%; Cr =95%; As = 93%), indicating a good overall accuracy of the methodology. The standard deviations of the measured heavy metal concentration were also in accordance with those in the standard reference material.

Statistical analyses

Pearson correlation coefficients and cluster analysis between trace metals and sediment quality parameters were worked out. Possibilities < 0.01 and < 0.05 (p<0.01 and

0.05) were considered statistically significant. All statistical analyses were performed using the computer software SPSS 17.0 for Windows (SPSS Inc.).

Results

Sediment Quality Characteristics

Table 1 shows the range, mean values and standard deviation of total organic carbon (%), percentage of sand, silt and clay and concentrations of Fe, Zn, Cu, Ni, Pb, Cd, Cr and As (mg Kg^{-1}, dw) in sediments of the five sampling stations.

Discussion

Heavy Metal Distribution

Spatial distribution of heavy metals in sediments of the estuarine environment is governed by geochemical and biogeochemical processes like sedimentation, precipitation, flocculation of particulate substances and by basin's hydrological condition (Che et al., 2003). In the present study, Fe was found to be the most prevalent metal which could be attributed to major role of basaltic trappean rocks and laterites contributing to the same (Sarkar et al., 2002). All metals except Zn and Cd exhibited maximum concentration at S5. The elevated value of Cu indicates that anthropogenic influence in the form of untreated domestic sewage is prevalent, as this element has a preferential association with organic matter (Hirner et al., 1990). Elderfield et al., 1979 opined that most trace metals precipitate with Fe forming polysulphide minerals, most commonly with Cu, Zn and Pb. Similar formation and precipitation of polysulphides can be the resultant effect of various factors in the S5 mangrove region. The organic carbon results show that the site receives a high load of organic matter which facilitates the formation of such polysulphides. S5 is located on the Matla, fed by the joint waters of The Bidyadhari, Khuratya and The Rampura. The site receives sewage discharge of Kolkata through the Bidyadhari River, besides being stressed due to intense human activities related to prawn aquaculture farms which supports the observed elevated values of most metals at this station. It may be mentioned that The Matla is gradually silting and drying at its upper reaches as it no longer receives freshwater inflow from the river Hooghly and it has become a tidal inlet of the sea. The region thus is inundated with sea water during high tides and the channel is almost completely drained of water during low tides resulting in the formation of extensive mudflats. Coupled with a weak ebb flow, the pollutants have a higher retention time resulting in their gradual deposition and accumulation (Sinha et al., 1998).

During the study, S1 showed the highest concentration of Zn, Ni and Cd. This estuarine area is primarily influenced by the presence of Haldia port-cum-industrial complex comprising of dock system, fertilizer project, refinery plant and petrochemical industries. The exponential trend of distribution of the aforesaid metals is thus a reflection of metal contamination due to the industrial activity in the vicinity besides inputs from the Damodar, Rupnarayan and Haldi rivers which drain the industrial belt of the hinterland of the estuarine region (De et al., 1985). High Cr contents in the sediment of the study area is due to the outfall of tannery effluents from the tanneries of the Bantala leather complex which release their wastes in the sewage canal along with organic matter and salt content (Sarkar et al., 2002**).** The observed high trend of Pb content in sediments might be ascribed to river borne sources (Förstner, 1983), intense human activities including agriculture and use of antifouling paints in the region

Table 1. Range (mean ± SD) of physico-chemical characteristics of sediments of the Sunderban estuarine region.

Parameters	Sampling Stations				
	S1	S2	S3	S4	S5
TOC (%)	0.81 – 0.96 (0.88 ± 0.07)	0.59 – 0.74 (0.67 ± 0.07)	0.46 – 0.60 (0.53 ± 0.07)	0.52 – 0.65 (0.58 ± 0.06)	0.8 – 1.4 (1.1 ± 0.3)
PSD (%) Sand	29.8 – 38.4 (43.3 ± 4.3)	64.8 – 74.3 (69.6 ± 4.7)	50.3 – 56.9 (53.6 ± 3.3)	17.8 – 24.6 (21.2 ± 3.4)	58.7 – 68.2 (63.6 ± 4.7)
Silt	33.9 – 42.3 (38.2 ± 4.2)	8.2 – 12.6 (10.3 ± 2.2)	15.7 – 20.7 (18.2 ± 2.5)	23.2 – 27.8 (25.5 ± 2.3)	7.6 – 12.8 (10.2 ± 2.6)
Clay	23.1 – 28.5 (25.8 ± 2.7)	15.9 – 22.1 (19.0 ± 3.1)	24.4 – 30.2 (27.3 ± 2.9)	49.8 – 55.6 (52.7 ± 2.9)	22.2 – 28.9 (25.5 ± 3.3)
Fe	33 680.54-41408.45 (37 539.85± 2864.95)	33 476.78 - 36479.36 (34 176.0 ± 1501.29)	30 156.89 – 34878.55 (32 534.38 ± 2361.0)	27022.28 – 32879.45 (29950.70 ± 2124.67)	36 249.65 – 42886.34 (39 567.94 ± 3318.34)
Zn	87.84 - 110.02 (98.83 ± 11.09)	61.23 – 77.01 (69.21 ± 6.2)	58.94 – 73.53 (66.22 ± 7.29)	54.32 – 68.56 (61.45 ± 7.12)	67.94 – 86.52 (77.25 ± 9.29)
Cu	45.45 – 56.02 (50.73 ± 5.28)	42.28 – 53.03 (47.68 ± 5.37)	37.79 – 46.67 (42.23 ± 4.44)	35.48 – 45.52 (40.65 ± 4.87)	46.89 – 62.23 (54.46 ± 7.67)
Ni	37.88 – 47.69 (42.78 ± 4.90)	32.16 – 40.77 (36.47 ± 4.30)	26.12 – 34.26 (30.26 ± 4.07)	21.38 – 29.46 (25.44 ± 4.04)	35.03 – 41.65 (38.30 ± 3.31)
Pb	41.06 – 50.03 (45.62 ± 4.48)	35.43 – 45.89 (40.67 ± 5.23)	33.98 – 41.18 (37.65 ± 3.60)	34.12 – 39.76 (36.93 ± 2.8)	43.89 – 53.35 (48.56 ± 4.73)
Cr	41.02 – 47.89 (44.46 ± 3.43)	34.28 – 44.52 (39.4 ± 5.12)	29.65 – 37.82 (33.57 ± 4.09)	24.89 – 33.24 (29.07 ± 4.17)	41.97 – 50.82 (46.35 ± 4.42)
Cd	2.98 – 4.02 (3.48 ± 0.52)	1.02 – 1.48 (1.28 ± 0.23)	BDL	BDL	2.03 – 2.47 (2.24 ± 0.22)
As	4.30 – 5.21 (4.75 ± 0.45)	2.79 – 3.43 (3.08 ± 0.32)	2.12 – 2.87 (2.53 ± 0.38)	0.77 – 1.65 (1.18 ± 0.44)	5.67 – 7.24 (6.44 ± 0.78)
Mean ± SD; TOC = Total Organic Carbon; PSD = Particle size distribution ; Fe = Iron ; Zn = Zinc; Cu = Copper; Ni = Nickel; Pb = Lead; Cr = Chromium; Cd = Cadmium; As = Arsenic					

(Alagarsamy, 2006; Monbet, 2006), auto exhaust emission and atmospheric deposition. Besides, factories located at the upper catchment of the Hooghly River and dealing with production of lead ingots and lead alloys are also major contributors of Pb in the sediments (Sarkar et al., 2007). It has been found that though As in sediments of the Bengal Basin is mainly geogenic in nature, yet various anthropogenic sources of As in sediments have been reported previously from the region (Sarkar et al., 2008; Chatterjee et al., 2009). The anthropogenic source of As in the Sunderbans have been identified to be derived from fertilizers, sewage sludge from urban settlements and from burning of cow dung cakes (Stull et al., 1986; Cornwell et al., 1996). Besides, a uniform pattern of distribution of As in the study area indicates that atmospheric deposition and addition of organic debris brought in by industrial outputs plays a major role in the study region (Leoni and Sartori, 1997; Leoni & Sartori, 1996).

US EPA Sediment Quality Guidelines

Sediments are classified as non-polluted, moderately polluted and heavily polluted, based on the SQG of US EPA (Perin et al., 1997).

Table 2. Elemental concentration (mg Kg^{-1}) of sediments, SQG by US EPA and Pollution Load Index (PLI) of metals in sediments of the sampling stations.

Elements	Sampling Stations					SQG		
	S1	S2	S3	S4	S5	Non-polluted	Moderately polluted	Heavily polluted
Fe	37539.85 (0.79)	34176.0 (0.72)	32534.38 (0.66)	29950.70 (0.63)	39567.94 (0.82)	ni	ni	ni
Zn	98.83 (1.03)	69.21 (0.73)	66.22 (0.69)	61.45 (0.64)	77.25 (0.81)	<90	90 - 200	>200
Cu	50.73 (1.12)	47.68 (1.05)	42.23 (0.93)	40.65 (0.90)	54.46 (1.21)	<25	25 - 50	>50
Ni	42.78 (0.62)	36.47 (0.53)	30.26 (0.44)	25.44 (0.37)	38.30 (0.56)	<20	20 - 50	>50
Pb	45.62 (2.28)	40.67 (2.03)	37.65 (1.88)	33.24 (1.66)	48.56 (2.42)	<40	40 - 60	>60
Cr	44.46 (0.49)	39.4 (0.43)	33.57 (0.37)	29.07 (0.32)	46.26 (0.51)	<25	25 - 75	>75
Cd	3.48 (11.6)	1.28 (4.26)	BDL	BDL	2.24 (7.46)	-	-	>6
As	4.75 (0.36)	3.08 (0.23)	2.53 (0.19)	1.18 (0.09)	6.44 (0.49)	<3	3 – 8	>8
PLI	1.12	0.84	0.62	0.53	1.04			
Values in parenthesis are the contamination factors; ni = not included; BDL = below detection level								

Table 3. EF values and I_{geo} of metals in sediments of the Sunderban estuarine region.

Metals	Sampling Stations				
	S1	S2	S3	S4	S5
Enrichment Factor					
Zn	1.13	1.0	1.01	1.0	0.95
Cu	1.44	1.43	1.35	1.34	1.44
Ni	0.78	0.71	0.66	0.57	0.64
Pb	2.85	2.61	2.61	2.61	2.85
Cr	0.57	0.57	0.52	0.47	0.57
Cd	14.6	5.87	----	----	9.0
As	0.44	0.32	0.28	0.14	0.62
I_{geo} value					
Fe	-0.34	-1.47	-0.59	-0.66	-0.28
Zn	-0.04	-0.45	-0.53	-0.64	-0.30
Cu	-0.16	-0.07	-0.10	-0.15	-0.27
Ni	-0.68	-0.91	-1.18	-1.43	-0.83
Pb	1.18	1.02	0.91	0.73	1.27
Cr	-1.02	-1.21	-1.43	-1.64	-0.97
Cd	3.53	2.09	---	---	2.89
As	-1.47	-2.12	-2.39	-2.42	-1.55

Table 4. Geo-accumulation Index proposed by Muller, 1979.

Pollution Intensity	Metal Accumulation	I_{geo} class
Very strongly polluted	> 5	6
Strongly to very strongly polluted	4 - 5	5
Strongly polluted	3 - 4	4
Moderately to strongly polluted	2 - 3	3
Moderately polluted	1 - 2	2
Unpolluted to Moderately polluted	0 - 1	1
Practically unpolluted	< 0	0

Table 5. TEL, PEL, ERL and ERM guideline values for trace elements[a,b] and mean quotients using the PEL and ERM values.

Element	S1	S2	S3	S4	S5	TEL	PEL	ERL	ERM
Fe	37539.85	34176.0	32534.38	29950.70	39567.94	n.i	n.i	n.i	n.i
Zn	98.83	69.21	66.22	61.45	77.25	124.0	271.0	150.0	410.0
Cu	50.73	47.68	42.23	40.65	54.46	18.7	108.2	34.0	270.0
Ni	42.78	36.47	30.26	25.44	38.30	15.9	42.8	20.9	51.6
Pb	45.62	40.67	37.65	36.93	48.56	30.2	112.2	46.7	218.0
Cr	44.46	39.4	33.57	29.07	46.35	52.3	160.4	81.0	370.0
Cd	3.48	1.28	BDL	BDL	2.24	0.68	4.2	1.2	9.6
As	4.75	3.08	2.53	1.18	6.44	7.2	41.6	8.2	70.0
m-PEL-Q	0.49	0.36	0.32	0.28	0.43	-	-	-	-
m-ERM-Q	0.28	0.21	0.20	0.17	0.25	-	-	-	-

[a] Long et al., 1995; [b] Concentrations are in mg kg^{-1} dry weight; n.i. = not indicated

Mean Concentration of heavy metals in sediments of Sunderban estuarine region is summarized in Table 2 and compared with the SQG of US EPA. Sediments are considered moderately polluted as per SQG with Cu, Ni, Cr at most stations and with As at S1 and S5.

Pollution Load Index (PLI)

Tomllinson's pollution load index (PLI) (Tomllinson et al., 1980) was calculated to understand the level of contamination with respect to heavy metals by computing the contamination factor (CF). CF of sediments of the study region was computed by considering the world average concentrations of these elements reported for shale as the background values (Turkian & Wedephol, 1961) by applying the following equations:

$$CF = \frac{C_{sample}}{C_{backgound}} \quad (1)$$

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times CF_4 \ldots\ldots CF_n} \quad (2)$$

Where,
CF = contamination factor
$\bar{C}_{sample}$ = mean metal concentration in sediments
$\bar{C}_{background}$ = mean natural background value of that metal
n = number of metals

Table 6. Pearson correlation matrix showing the relationship between the trace elements and sediment quality parameters of the five stations of the Sunderban wetland.

	Fe	Zn	Cu	Ni	Pb	Cr	Cd	As	Sand	Silt	Clay	TOC
Fe	1											
Zn	0.921*	1										
Cu	0.993**	0.916*	1									
Ni	0.877	0.642	0.877	1								
Pb	0.997**	0.936*	0.983**	0.848	1							
Cr	0.948*	0.993**	0.952*	0.708	.954*	1						
Cd	0.883*	0.643	0.855	0.948*	0.871	0.689	1					
As	0.977**	0.961**	0.969**	0.82	.980**	0.975**	0.796	1				
Sand	0.496	0.497	0.58	0.537	0.447	0.564	0.266	0.556	1			
Silt	-0.046	-0.283	-0.142	0.161	-0.025	-0.297	0.363	-0.138	-0.68	1		
Clay	-0.568	-0.44	-0.625	-0.751	-0.515	-0.52	-0.501	-0.6	-.916*	0.332	1	
TOC	-0.926*	-0.990**	-0.935*	-0.685	-0.930*	-0.996**	-0.643	-0.968**	-0.614	0.358	0.555	1

***Correlation is significant at the 0.05 level (2-tailed); ** Correlation is significant at the 0.01 level (2-tailed)**

Cluster analysis

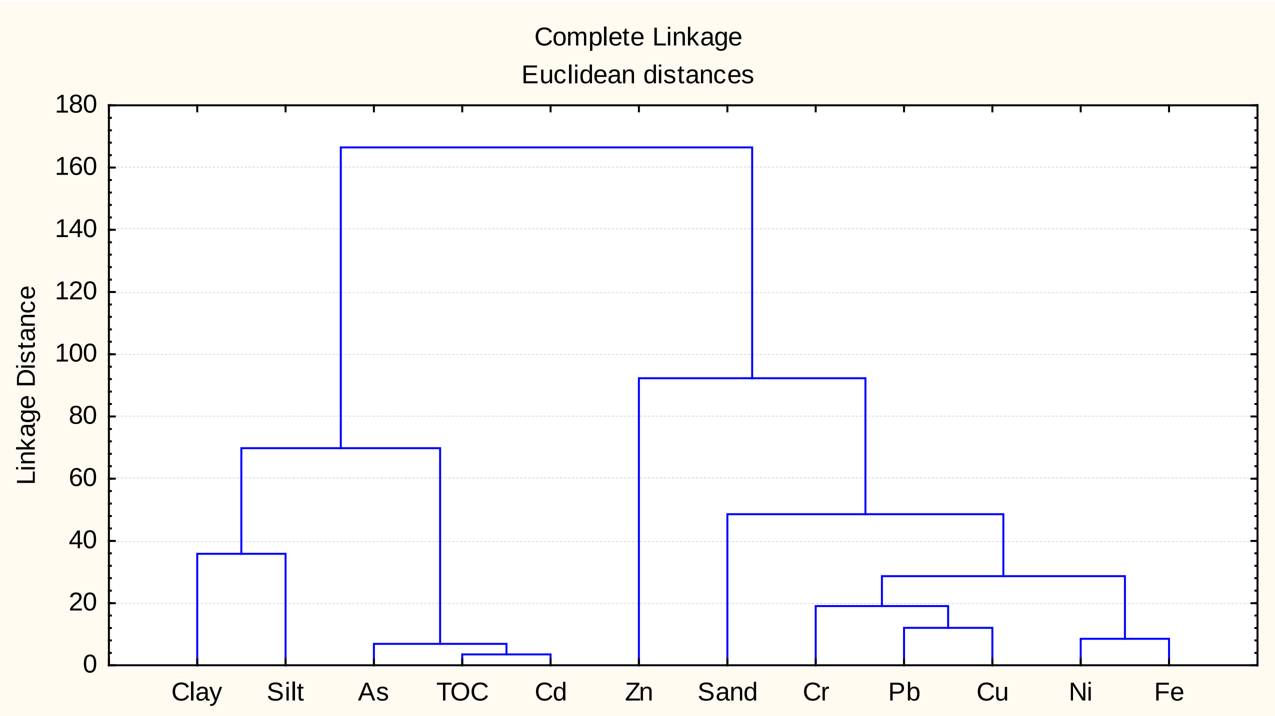

Fig. 2. Dendogram showing the relationship between sediment samples in the Sunderban estuarine region.

The PLI represents the number of times by which the metal content in the sediment exceeds the average natural background concentration and gives a summative indication of the overall level of heavy metal toxicity in a particular sample (Essien et al., 2009). The PLI value of >1 indicates pollution whereas < 1 indicates no pollution. The contamination factor and pollution load index are given in Table 3. Results show that CF values of Zn (at S5), Cu (in S1, S2 and S5), Pb (at all stations) and Cd (at S1, S2 and S5) exhibit values of >1. This may be due to external contamination loading arising from sources like industrial and agricultural runoff and other anthropogenic inputs. The values of pollution load index (Table 2) were greater than unity (>1) in the sediments of S1 and S5 which reveal that they are of pollution concern in view of the present land use practices.

Enrichment Factor and Index of Geo-Accumulation

Enrichment factor and Index of Geo-Accumulation are good tools to assess the relative contribution of natural and anthropogenic inputs of metal into the sediments. This technique has been well applied in several studies to assess metal contamination in marine sediments (Khaled et al., 2006; Acevedo-Figueroa et al., 2006; Ghrefat et al., 2006). In this work EFs were computed by normalising with Fe (Blomqvist et al., 1992) because Iron remains conservative during diagenesis (Berner, 1980) and its geochemistry is similar to most metals both in oxic and anoxic conditions. Besides, natural concentrations of Fe in sediments are uniform and beyond the influence of humans thereby justifying its use as a normaliser (Daskalakis and O'Connor, 1995).

Mathematically, EF is a concentration ratio of measured metal to iron in the sample of interest divided by the background metal/iron background concentration ratio. EF is expressed as:

$$EF = \frac{(X/Fe)_{sediment}}{(X/Fe)_{background}} \quad (3)$$

Where, $(X/Fe)_{sediment}$ is the ratio of heavy metal (X) to Fe in the sample of interest, and $(X/Fe)_{background}$ is the natural background value of the metal Fe ratio. Because we do not have Fe and heavy metal background values for our study area, the average crust metal values from Turekian and Wedepolh, 1961 (Khaled et al., 2006) were adopted for the calculation of EF.

EF values were interpreted as suggested by Birth, 2003, where EF <1 indicates no enrichment; 1-3 is minor; 3-5 is moderate; 5-10 is moderately severe; 10-25 is severe; 25-50 is very severe; and > 50 is extremely severe.

EF values for metals in sediments are presented in Table 3. Most metals exhibit no to minor enrichment except Cd, which show severe enrichment at S1 and moderately severe enrichment at S5. It may be noted that S1 is located close to the port cum industrial hub at Haldia which accounts for its high levels of Cd. Higher levels of Cd at S5 may be due to anthropogenic influence due to intense land use pattern associated with boating activities, aquaculture and agriculture.

The I_{geo} values for the metals studied were calculated using the Muller's, 1979 expression: $I_{geo} = \log_2\left(\frac{C_x}{1.5B_x}\right)$ (4)

Where,

C_x is the measured value of metal X and

B_x is the natural background concentration of metal X (Turkian KK, Wedephol, 1961).

The I_{geo} value of the metals studied is presented in Table 3. It is found that the I_{geo} value of most stations belong to I_{geo} class 0 (Table 4) indicating no pollution. The I_{geo} class of S1 and S5 is 3 indicating moderate to strong pollution levels with respect to Cd, thus corroborating the earlier findings of pollution levels based on enrichment factor.

Ecotoxicological Assessment of Heavy Metal Concentrations in Sediments

Two sets of Sediment Quality Guidelines (SQGs) developed for marine and estuarine sediments (MacDonald et al., 2000; Long & MacDonald, 1998) were used in this study for ecotoxicological assessment of heavy metal concentrations in sediments of the study site. They are (1) Effect range low (ERL)/ Effect range median (ERM) and (2) Threshold effect level (TEL)/ Probable effect level (PEL). Low - range values (i.e. ERLs or TELs). ERLs and TELs are intended as concentrations below which adverse effects upon sediment dwelling fauna would be only infrequently observed. In contrast, the ERMs and PELs represent chemical concentrations above which adverse effects are likely to occur (Long & MacDonald, 1998).

Table 5 shows the comparison of the metal contaminant in sediments from which concentrations where adverse biological effects are expected to occur rarely (< TEL/ERL), occasionally (≥TEL/ERL and <PEL/ERM) and frequently (≥PEL/ERM) can be known. It is found that Zn, Cr and Cd in all sediment samples were in the minimal effect range (< TEL/ERL); Cu, Pb and As were at concentrations at which biological effects are expected to occur occasionally (≥TEL/ERL and <PEL/ERM) while Ni showed concentrations above ERM at S2, S3 and S5.

In order to determine the possible biological effect of combined toxicant groups, mean quotient calculable from the two empirically derived set of SQGs using PEL and ERM values were used. The mean ERM quotient (*m*- ERM - *Q*) has been calculated according to Long et al., 1998 as follows:

$$m - ERM - Q = \frac{\sum_{i=1}^{n}(C_i/ERM_i)}{n} \qquad (5)$$

Where,

C_i is the sediment concentration of compound *i*,

ERM_i is the ERM for compound *i* and

n number of compound *i*.

Similarly, the mean PEL quotient (*m* – PEL - *Q*) can be calculated according to the equation:

$$m - PEL - Q = \frac{\sum_{i=1}^{n}(C_i/PEL_i)}{n} \qquad (6)$$

Where, PEL*i* is the PEL of compound *i*.

Mean ERM and PEL quotients have been related to probability of toxicity based on the analysis of matching chemical and toxicity data from 1068 samples from the USA estuaries (Long & MacDonald, 1998; Long & MacDonald, 2000). According to this classification, all the sediment samples studied can be classified as "Medium-low priority sites" with 30% probability of toxicity with respect to mean ERM quotients and 25% probability of toxicity with regard to mean PEL quotient. It can be inferred thus that the possible biological effect of combined toxicant group in the study site is of concern. However, this provides an informal interpretive tools or benchmark to provide a basis for evaluating the risks posed to sediment dwelling organisms by sediment associated contaminants.

Correlation coefficient

The correlation coefficient of elements and sediment quality parameters were analysed to study the inter-elemental associations and to understand the behavior of metals during transport and distribution in the mangrove ecosystem. It was found that Fe exhibits strong and significant correlation with all other metals which suggest that it is the prime controlling factor in precipitation and redistribution of the metals by adsorption of these elements by amorphous Fe-oxyhydroxides. All the elements show a high degree of correlation with each other, indicating their identical behavior during transport in the estuarine environment. A significant observation in the correlation matrix is that sand is found to show associations with all the metals while a weak association is found between the metals and finer sediment fractions, namely silt and clay. This suggests that these finer fragments do not play a significant role in distribution and sedimentation of metals in the estuarine region and other processes like biological effects and external inputs have resulted in the non significant correlation observed. Besides, TOC is found to correlate negatively and significantly with all the studied elements indicating that it neither plays any role as metal concentrators nor does it has any role in the distribution pattern of the metals in the region.

In order to have a better understanding on the main controlling factors that determine the distribution of metals and other variables in the study region, cluster analysis was performed using complete linkage and Euclidean distance (Fig.2). The cluster formed by the variables was represented by means of two dimensional dendograms which bring out the relation between the clusters. The primary aim of the technique was to reduce the data set to infer possible relationship between the variables. Results show the formation of three distinct clusters. The dendograms are found to mirror the observation found in the correlation matrix. However, association of variables didn't vary much at each site. It was found that only Fe contributed to metal distribution, which is in consonance with the results of the correlation matrix. This suggests that the metals are transported to the mangrove region quite independently. It can therefore be concluded that that sediments in the study region have similar chemical characteristics. On the whole, differences in area, volume and retention time of water might be responsible for the observed differences in association among the different variables studied. This indicates that the metal deposition in sediments portrays the general influence of anthropogenic factors that occur in the mangrove environment. We can thus summarise that human influence has masked the actual elucidation of the processes involved in metal association and deposition in the Sunderban estuarine region.

Conclusion

The study carried out in the intertidal Sunderban estuarine region reveal that spatial distribution of metals in sediments are influenced by various processes like sedimentation, precipitation and flocculation. The combined use of different methods to compute sediment metal contamination was undertaken to comprehensively interpret sediment characteristic and to construe ecotoxicological risk. Our results suggest that Nayachar (S1) and Canning (S5) stations of the estuarine region is getting polluted, showing a PLI value of >1. Besides, the enrichment pattern of Cd suggests their extraneous anthropogenic source. The study forefronts the ecotoxicological risk posed to benthic organisms in the region in the recent future if the present level of anthropogenic loading of metals is continued. In conclusion, it is proposed that a frequent monitoring programme of the region be undertaken to ascertain the long term effect of these heavy metals of anthropogenic origin. This would yield twin benefits of ascertaining the risk associated with current scale of developmental activities and the required level of preparedness necessary to maintain this ecoregion in sound health.

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