SEQUENTIAL EXTRACTION FOR THE SPECIATION OF TRACE HEAVY METALS IN HOOGHLY RIVER SEDIMENTS, INDIA

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Abstract

 The spatial variation of metal concentrations in the sediments is associated with the level of pollution along river stretches. Thus, the chemical speciation of seven trace heavy metals (Co, Cd, Cr, Cu, Ni, Pb and Zn) in Hooghly River sediments from four sampling locations was determined using the modified BCR sequential extraction procedure. The studied sediments were observed to be highly heterogeneous in their textural characteristics, showing wide differences in grain sizes. On average 93% Pb, 70% Co, 62% Cd and 55% of total Cu were estimated to be partitioned with the first three labile sequential extraction phases. As these fractions are readily bioavailable, they may influence negative biological effects in their concerned aquatic ecosystem. The presence of Ni, Cr and Zn in high proportion within the residual section (58–82%) and their simultaneous low levels in the exchangeable fraction indicated that the analyzed sediments were relatively unpolluted with Ni, Cr and Zn. The presence of exchangeable Cd (27%) at Diamond Harbor sampling point is a serious threat to the Sundarban National Park, which is also notified as a (Royal Bengal) Tiger Reserve, a Biosphere Reserve and an UNESCO World Heritage Site.

Keywords: Heavy metal fractionation, Hooghly River, River sediments, Speciation.

Introduction

 In many developing nations including India the mushrooming urban agglomerates and growing industrial hubs continue to cause all types of pollutions of the worst order. Among the pollutants trace heavy metals being persistent and non-biodegradable are responsible for various critical environmental pollution problems worldwide (Yuan et al., 2004). Hence identification, determination and monitoring of specific chemical forms of trace heavy metals responsible for toxicity

are extremely important (Tokalioglu et al., 2000). River sediments, one of the basic environmental components of the riverine ecosystem, act as the principal source of heavy metals in this aquatic ecosystem (Gale et al., 2006). Sediments govern the storage and transport of metals to the surrounding environment (Cuong and Obbard, 2006). The four factors that regulate the distribution of metals in natural water bodies are the substrate sediment composition, the suspended sediment composition, association of metals with various geochemical phases in sediments and the water chemistry (Morillo et al., 2004; Mohiuddin et al., 2011). Various natural processes (such as weathering of rocks and minerals, flow of water, current, mixing of water with sea, etc) as well as anthropogenic activities (such as discharge of untreated or partially treated sewage and effluent, disposal of solid waste, mining, agrichemical runoff, vehicular movements, oil leakage, prawn and fish aquaculture, etc) are responsible for sedimentation of heavy metals in rivers.

After their introduction in aquatic environment metals are adsorbed into inorganic and organic particulates, get deposited and produce elevated metal concentrations (Jeon et al., 2003; Ochieng et al., 2007). But, some of the sediment-bound metals may remobilize to water via the variation in environmental conditions (such as acidification, redox potential change, organic ligand levels, etc.) and may further impose adverse effects on living organisms (Rauret, 1998; Liu et al., 2009). According to Mohiuddin et al., (2010;2011) the accumulation and distribution of trace heavy metals in river sediment are affecting aquatic organisms at an alarming rate.

Adverse effects include skin lesions, increased tumor frequency and reproductive toxicity in fish, reproductive failure in fish-eating birds and mammals, and decreased biodiversity in aquatic ecosystem (Lasheen and Ammar, 2009). Moreover, these persistent toxic chemicals can be bioaccumulated in fish and hence put threats to human health even after contaminants are no longer released from point or non-point sources (Mulligan et al., 2001; Lasheen and Ammar, 2009).

Heavy metals are considered to be suitable indicator for aquatic pollution. But, the total metal concentration in sediments is now conceived as not a true indicator of toxicity assessment to aquatic organisms (Tokalioglu et al., 2000). This is because use of total concentration as a criterion to evaluate the potential effects of sediment contamination implies that all forms of a given metal have an equal impact on the environment; such an assumption is clearly untenable (Tessier et al., 1979). The heavy metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena impacting their reactivity, mobility and thus, bioavailability (Mohiuddin et al., 2011; Nouri et al., 2011). Hence, the possibility for overestimation of exposure risk associated with trace heavy metal pollution can be minimized by systematic sequential extraction technique. Moreover, the prediction of the environmental impacts of trace heavy metals can be assessed far accurately using the speciation study. Speciation studies have been widely carried out to evaluate the origin, mode of occurrence, biological and physiochemical availability, mobilization, and transport of trace heavy metals in river sediments

utilizing the Community Bureau of Reference (BCR) method, proposed by the Standards Measurements and Testing (SM and T) (Davutoglu et al., 2008; Fan et al., 2008; Lasheen and Ammar, 2009; Liu et al., 2009; Mohiuddin et al., 2011; Nouri et al., 2011; Oyeyiola et al., 2011; Dundar et al., 2012).

The Hooghly River represents final part of the River Ganges before flowing into the Bay of Bengal. It is the only river flowing beside Kolkata, one of the largest metropolitan cities of India of about 4.5 million populations (Census, 2011). The demand for water from the river is continually increasing due to exponential population growth, irrigation and industrial developments. But, the river has become highly polluted as a consequence of intensive anthropogenic activities (Purushothaman and Chakrapani, 2007).

The major water pollution is contributed by more than 100 industries comprising 55 jute mills, 6 power stations, 6 pulp and paper, 4 cotton textiles, 3 oil storage (petroleum), 3 paint and varnishes, 3 hydro-generated vegetable oil and soaps, 2 metal and steel, 2 distilleries, one each of viscose rayon, yeast, tannery, rubber, polythene, chlorine, insecticide (BHC), safety match, phosphate fertilizer, spreading on both the banks of the Hooghly River. Moreover, failure of the authority in implementing the multibillion 'Ganga Action Plan' to rejuvenate the water quality has deteriorated the biodiversity further (Dudgeon, 2005). This study was aimed to determine the total concentrations as well as the chemical speciation of seven trace heavy metals (Co, Cd, Cr, Cu, Ni, Pb and Zn) in Hooghly River sediments by the modified BCR sequential extraction procedure (Kartal

et al., 2006). This study would help to evaluate mobility, impact and the possible bioavailability of the investigated trace heavy metals in the Hooghly riverine and the Sundarban estuarine ecosystems.

Materials and Methods
Study area

The Hooghly River is an approximately 260 km long distributaries of the River Ganges in West Bengal, India with a mean sediment load of 65.19×10^6 t (Mukhopadhyay, 2007). It splits from the Ganges at the Farakka Barrage and at Nurpur it enters an old channel of the Ganges and turns south to empty into the Bay of Bengal. In the present study triplicate sediment samples were collected from selectively chosen four locations along 134 km stretch of Hooghly River between January and March in 2016 (Fig. 1).
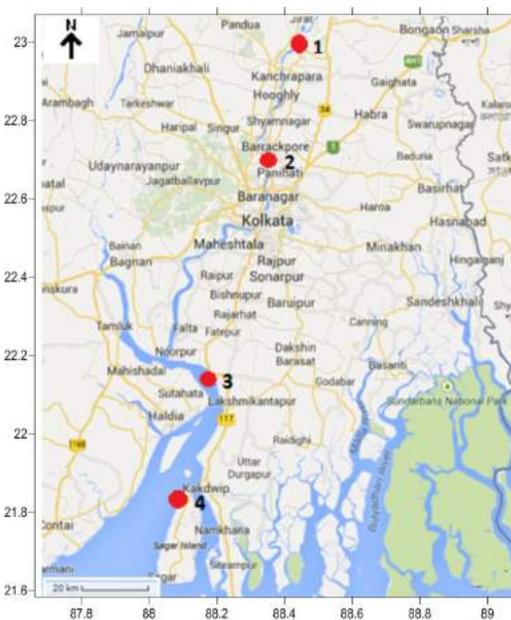

Fig. 1. Location of the four sampling sites (1. Tribeni, 2. Barrackpore, 3. Diamond Harbor, and 4. Gangasagar) of the Hooghly River, West Bengal, India.

The details of the sampling locations are given in the Table 1. Tribeni and

Barrackpore are at the middle stretch of the Hooghly River with medium water currents (fresh water ecosystem) while Diamond Harbor and Gangasagar are situated near the confluence points of the river with Bay of Bengal, where water currents are strong and sea water is well mixed (estuarine ecosystem). Moreover, Diamond Harbor is at the Sundarban National Park, which is also marked as a (Royal Bengal) Tiger Reserve, Mangrove Biosphere Reserve and an UNESCO World Heritage Site.

Sample collection and preparation

Triplicate sediment samples were collected from the river bed at a depth of 0−15 cm using an Ekman Grab bottom sampler of stainless-steel. Without emptying the dredge sub-samples were collected from the centre with a polyethylene spoon to avoid any contamination by the metallic parts of the dredge. Then the samples were introduced into the polyethylene bags cleaned by washing first with tap water and then HNO_3 (1:1) and finally with distilled water. At first the samples were stored at 4^0C in a refrigerator before the drying step only and then dried at 45^0C in an electrical oven for 48 h. They were subsequently ground in an agate mortar, sieved (aperture of 270 meshes), homogenized by coning and quartering and then stored in polyethylene bags in a desiccators with calcium chloride to avoid contamination throughout the analyses. The fraction of lower than 270 mesh (<53 μm) of the sediment samples was used for analysis (Tokalioglu et al., 2000). Finally, the total metal contents and speciation of Co, Cd, Cr, Cu, Ni, Pb and Zn were measured in the sediment samples. All glassware and plastic containers were washed with 15% HNO_3 and rinsed thoroughly with de-ionized water. All standard and reagent solutions were stored in polyethylene bottles.

Sequential extraction method

The sequential extraction method (Kartal et al., 2006) was applied to sediment samples to partition them among fraction 1 (Exchangeable, water and acid-soluble fraction−bound to carbonates), fraction 2 (Reducible fraction−bound to Fe and Mn oxides), fraction 3 (Oxidizable fraction−bound to organic matter and sulfides) and residual fraction (strongly associated to the crystalline structures of the minerals).

Sample analysis

After the four fractionation processes applied sequentially, the extracts acquired were evaporated almost to dryness. Then the last volume (except the oxidizable fraction that was made up to 5 ml) was made up to 2 ml with 2 mol/l HNO_3. Finally the concentrations of Co, Cd, Cr, Cu, Ni, Pb and Zn in the acquired extracts were determined by Flame Atomic Absorption Spectrometer (Perkin Elmer AAnalyst 400) using the injection method (Elci et al., 1990). The precision of the method was controlled by including blanks, duplicate samples and the method of standard addition (Fytianos and Lourantou, 2004). As a quality assurance measure, each sediment sample was subjected to triplicate analyses and the measurements are given as mean.

Results and Discussion
Physicochemical characteristics of sediments

Data for pH, organic carbon content (%)

**Table 1. Name and features of the different sampling sites of the Hooghly River.**

Sample No.	Location	Features
1	Tribeni, Kalyani	Bandel thermal power plant discharge, brick-kilns, agrochemical runoff, sewage disposal, immersion of idols.
2	Barrackpore	Diesel motor boat ferry services, jute mill effluent, immersion of idols, bathing, sewage disposal.
3	Diamond Harbor, Sunderban National Park	UNESCO World Heritage Site, Prawn cultures, fishing, tourist activity, diesel motor boat ferry services.
4	Gangasagar, Sagar Island	Pilgrim activity, tankers, bathing, motor boat ferry services, fishing, aquaculture, immersion of idols.

Table 2. Physicochemical characteristics of the Hooghly River sediments.

Sampling sites	pH	Sand (%)	Silt (%)	Clay (%)	Organic carbon (%)
Tribeni	7.1	23	8.3	69	2.2
Barrackpore	6.5	25	13	62	0.89
Diamond Harbor	7.2	44	8.7	47	1.3
Gangasagar	7.8	61	9.7	28	0.14

Table 3. Total metal concentrations (mg/kg) in sediments at different sampling sites of the Hooghly River.

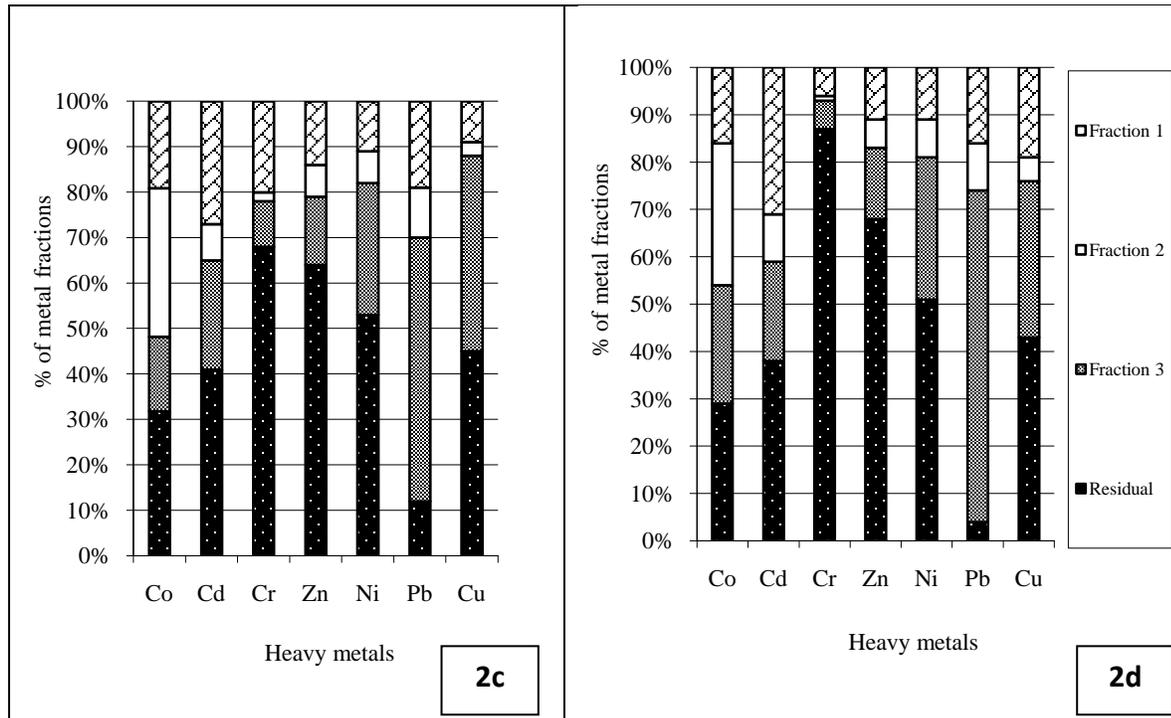| Sampling sites	Total metal concentrations (Mean ± SD) in mg/kg						
	Co	Cd	Cr	Zn	Ni	Pb	Cu
Tribeni	7.8 ± 1.1	0.91 ± 0.12	25 ± 3.7	59 ± 7.6	66 ± 4.8	6.9 ± 1.1	30 ± 5
Barrackpore	9.4 ± 1.9	1.3 ± 0.09	38 ± 2.91	72 ± 8.1	56 ± 7.5	25 ± 3.9	49 ± 3.3
Diamond Harbor	5.2 ± 1.3	0.78 ± 0.06	47 ± 3.3	64 ± 7.2	72 ± 6	30 ± 4.8	44 ± 7.1
Gangasagar	14 ± 2.7	0.65 ± 0.11	30 ± 4	70 ± 9.3	77 ± 5.9	18 ± 1.7	38 ± 3.7
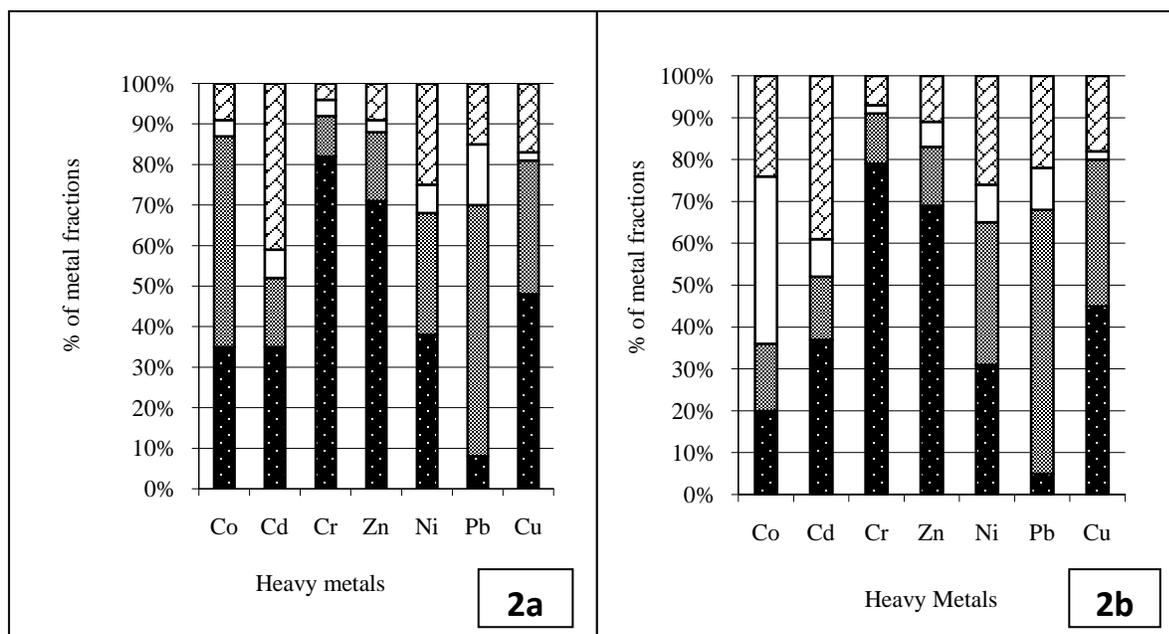
Fig. 2. Speciation of trace heavy metals in the Hooghly River sediments at **(a)** Tribeni, **(b)** Barrackpore, **(c)** Diamond Harbor and **(d)** Gangasagar.

and texture analysis of the sediments used for sequential extraction are shown in Table 2. The results showed that the sediments of the studied sampling sites were characterized by marginally acidic to slightly basic pH (6.5–7.8). Sand was present in higher concentration at the confluence point (Gangasagar, 61%) as compared to the other sites while clay dominates in Tribeni (69%), which is least flooded by tides (Fig. 1). The sediments showed low organic carbon content (0.14–2.2%), representing a typical torrential river environment. The lowest organic carbon content (0.14%) was observed in Gangasagar, which might be due to the continuous flooding activity of the coastal tides.

Total metal concentrations in sediments

Total contents of Co, Cd, Cr, Zn, Ni, Pb and Cu in the sediments at different sampling sites along the Hooghly River are presented in Table 3. On an average metal concentrations were found to decrease in the order Ni> Zn> Cu> Cr> Pb> Co> Cd. Higher concentrations of Ni and Zn in river sediments might be due to different anthropogenic sources including industrial discharges (Goh and Chou, 1997). Prominent contents (mg/kg) of Cu (310–5,214), Cr (223–5,167) and Co (113–624) were reported to be present in the upper stretches of the river Ganges (Purushothaman and Chakrapani, 2007). Those reported values are in contrast to the present finding of relatively lower contents of the metals (30–49, 25–47 and 5.2–14 mg/kg, respectively) in the Hooghly River sediments. Atmospheric deposition of exhaust particulates from the large volume

of motor-boats, used for ferry services in Barrackpore, Gangasagar and Diamond Harbor, may be responsible for elevated level of Pb (25, 18 and 30 mg/kg, respectively) in studied sediments. Comparatively low Cd concentrations were found in all the sampling sites (0.65–1.3 mg/kg). Overall, total metal concentrations in the Hooghly River sediments can be regarded as relatively low when compared to the reported levels of metals in upstream sediments of the river Ganges.

Speciation of metals in sediments

Speciation of the studied seven trace heavy metals in the Hooghly River sediments are shown in the Fig. 2. Speciation of sediments at Tribeni revealed that 52% Co (3.32 mg/kg) was present in the oxidizable fraction while at other three sampling sites appreciable amount of Co (30–40%) was observed as reducible, bound to Fe and Mn oxides. Generally, the Fe-Mn colloids constitute a significant sink for heavy metals in the aquatic environments (Purushothaman and Chakrapani, 2007). Moreover, the high scavenging efficiencies of Fe and Mn oxides is reported to be responsible for their binding with Co (Dundar et al., 2012). The colloids accumulate metals from the aqueous system by the mechanism of adsorption and co-precipitation (Bordas and Bourg, 2001). The present finding is concurrent with the observations reported by Dundar et al., (2012) but, is in contrast with the observation by Tokalioglu et al., (2000), where the authors reported that Co was mostly associated with the oxidizable fraction as compared to the reducible or residual fractions.

Different partitioning pattern of Cd was observed in the different sediment samples. Cd was detected to be present relatively at higher levels both in the exchangeable (27–41%) and residual (35–41%) fractions in all sampling locations. It reflects that a portion of total Cd in this segment of the Hooghly River is mobile and potentially more bioavailable in sediments while another prominent portion is strongly associated with the crystalline structures of the minerals and thus, not labile. Presence of Cd in the exchangeable fraction at higher level was previously reported by Guevara-Riba et al., (2004) while its presence mostly in the residual fraction was reported by Lasheen and Ammar (2009). Moreover, Cd was observed to be almost absent in the reducible fraction (7–10%), thus presence of Cd bound to Fe and Mn oxides of the study area can be concluded to be low. A similar observation was reported by Cuong and Obbard (2006). Higher Cd concentration was reported to be related with industrial emission, atmospheric deposition, metal plating, paints and leachates from defused Ni-Cd batteries (Mohiuddin et al., 2011; Dundar et al., 2012). The presence of exchangeable Cd (27%) at Diamond Harbor is a threat to the Sundarban National Park.

The bioavailability of an element decreases with decreasing the order of chemical phases from the exchangeable to the residual fractions (Dundar et al., 2012). In the present study Cr was detected to be present at the highest level in the residual (68–87%) fraction and the lowest level in the exchangeable fraction (~9.3%) in all sampling sites, inferring that Cr was present as the least bioavailable form in sediments. This finding is in agreement with the previous observations by Guevara-Riba et

al., (2004) and Cuong and Obbard (2006). The results indicated that in the study area Cr was embedded in the crystal lattice of the sediment fraction and was unavailable for remobilization except under very harsh condition (Dundar et al., 2012). Thus, in the study area the sediment was estimated to be relatively unpolluted with Cr and environmental risk from Cr can be considered to be negligible.

Zinc was witnessed to be dominant in the urbanized Barrackpore sampling point (72 ± 8.1 mg/kg; Table 3), which was close to the Kolkata megacity. In all the sampling locations the dominant chemical form of Zn was extracted from the residual fraction (64−71%), generalizing that Zn was strongly associated to the crystalline structures of the minerals of sediments in the studied stretch of the Hooghly River. Thus, Zn was the least mobile and thus was not readily available for biological uptake in the studied aquatic environment. The second highest concentration of Zn was discovered in the oxidizable fraction (14−17%). This might result from the untreated or partially treated sewage discharge (Mohiuddin et al., 2011), motor boat ferry services (Sorme et al., 2002) and due to discharge from prawn culture (Cuong and Obbard, 2006).

The highest occurrence of Ni was noticed in the residual fraction (38−53%) in all the sampling locations other than Barrackpore where the highest percentage was found in the oxidizable fraction (34%). From the results it appeared that most of the Ni was associated with the detrital silicate minerals present in the residual fraction (Lasheen and Ammar, 2009). Thus, most of the Ni was strongly bound to sediments and was unavailable for biota. Similar results were previously reported from Spain (Morillo et

al., 2004) and Singapore (Cuong and Obbard, 2006) river sediments. The presence of Ni in less mobile phases suggested that the trace metal had lower environmental risk in the study area.

Lead is classified as a probable human carcinogen (Adriano, 2001). Moreover, Pb is considered to be a good indicator of traffic related pollutant sources or battery recycling plants, and also of pollution by urban runoff water (Mukai et al., 1994). In the present study Pb was found to be mostly present in the oxidizable fraction (58−70%). This is in agreement with the earlier findings by Tokalioglu et al., (2000) but, is in contrast with the observations by Yuan et al., (2004) and Cuong and Obbard (2006), in which the authors reported that Pb was mostly partitioned in the residual fraction. The presence of Pb mostly bound to organic matter and sulfides might be from motor boat ferry services (Mukai et al., 1994), metal plating, immersion of idols (coated with paints containing high amounts of Pb) (Dundar et al., 2012) in the study area. Organic matters with high molecular weight acids have been shown to play an important role in the distribution and dispersion of Pb by chelation and cation exchange processes (Purushothaman and Chakrapani, 2007).

Copper was observed to be partitioned equitably between the oxidizable (33−43%) and the residual (43−48%) fractions. Hence, a large portion of Cu was bound to organic matter and sulfides, and another prominent segment was strongly associated with the crystalline structures of the minerals. The finding of higher presence of Cu in the oxidizable fraction in the present study is concurrent with the previous observations by Tokalioglu et al., (2000), Morillo et al.,

(2004) and Cuong and Obbard (2006) while that in the residual fraction is in agreement with the findings by Lasheen and Ammar (2009). According to Morillo et al., (2004) the high stability constant of organic Cu compounds results in formation of stable complexes between Cu and organic matters. High level of Cu was reported to be originated from sewage and effluent discharge in water bodies (Mohiuddin et al., 2011).

Conclusions

The sequential extraction technique was applied to the Hooghly River sediments to determine the potential mobility and the possible transfer of the seven trace heavy metals (Co, Cd, Cr, Cu, Ni, Pb and Zn) from sediments to the surrounding aquatic ecosystem. Among the studied metals, Cd was found to have the highest mobility while Cr was the least mobile in sediments. The extent of pollution in the studied sediments implied that the scenario was much dreadful with respect to the trace heavy metals Pb, Co, Cd and Cu, and might severely affect the aquatic ecology of the river. The most likely anthropogenic sources of pollution were motor boat ferry services, metal plating, immersion of idols, industrial emission, atmospheric deposition, paints, leachates from defused Ni-Cd batteries, and discharge of untreated or partially treated sewage into the river.

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