

Heavy Metal Deposition in Some Brackishwater Ponds of Sunderban (India) During Off-season of Shrimp Culture

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Abstract

Spatial and temporal variations of heavy metal deposition were identified in some brackishwater shrimp ponds of the Sunderban (India) during off-seasons (November to May). Samples of water and sediment were collected from five different localities during November-December and April-May and were analyzed for metals (Cd, Zn, Pb and Fe) by atomic absorption spectrophotometry. The concentrations of all these metals showed significant variations in water and sediment, except Zn in water. Variation among localities was significant only in water Cd and in sediment Pb and Fe. Heavy metal concentrations were unrelated to physico-chemical variables evaluated. Impact of drainage pattern on spatial variations of the metals is discussed.

Introduction

Low lying areas in the mangrove delta of Sunderban (India), which are periodically inundated by tidal water, are widely used for cultivation of various penaeids, chiefly *Penaeus monodon* (Ray 1993). Post larvae of *P. monodon* (PL20 – PL25, locally known as 'pin') are stocked in temporary earthen embankments (locally known as 'bheris') at the start of the monsoon and are harvested after 90 to 100 days. After the culture of *P. monodon*, these water bodies are generally left for three to four months during the post-monsoon period to support minor crustaceans and brackishwater fish and then before the next monsoon they are drained and dried to prepare for the next *P. monodon* crop.

Most of these water bodies receive moderate to large loads of domestic sewage and industrial wastes carried through the Hooghly estuary. Kolkata city sewage mixed with effluents of various small-scale industries contributes

a significant load of metallic effluents to the Hooghly estuary. Bhowal et al. (1987) detected 11 to 190 $\mu\text{g}\cdot\text{g}^{-1}$ Pb and 62 to 809 $\mu\text{g}\cdot\text{g}^{-1}$ Zn in the sludge of Kolkata city sewage. Effluents of tanneries situated in east Kolkata have been found to contain 0.39 to 0.72 $\mu\text{g}\cdot\text{mL}^{-1}$ Pb, 0.18 to 0.30 $\mu\text{g}\cdot\text{mL}^{-1}$ Zn and 2.9 to 4.3 $\mu\text{g}\cdot\text{mL}^{-1}$ Fe (Chattopadhyay et al. 2000). These effluents are mixed with city sewage and are finally discharged into the network of Hooghly estuary. Deb and Santra (1997) observed that fish cultured in Kolkata city sewage fed ponds accumulated 0.41 to 0.46 $\mu\text{g}\cdot\text{g}^{-1}$ Pb and 1.01 to 1.03 $\mu\text{g}\cdot\text{g}^{-1}$ Zn in their body. Apart from city sewage of Kolkata and Howrah, the Hooghly estuary receives metallic effluents from huge number of industries situated on its either side (Kaviraj 1989). Large quantity of metal ions thus accumulate daily in the estuary and, carried downstream, are deposited over vast low lying areas of Sunderban. Gastropod *Nerita articulata* collected from Sagar island situated in the lowest stretch of Hooghly estuary showed 40 to 98 $\mu\text{g}\cdot\text{g}^{-1}$ Zn and trace amount to 8.8 $\mu\text{g}\cdot\text{g}^{-1}$ Pb in their body (Mitra and Chaudhury 1993a). Ghosal et al. (1997) observed that in some brackishwater ponds of Kakdwip and Tona, situated in the southern part of Sunderban along the lower stretches of Hooghly estuary, heavy metal concentrations in water exceeded the maximum permissible limit of WHO for drinking purpose and resulted in accumulation of the metals at a very high concentration in fish ($> 200 \mu\text{g}\cdot\text{g}^{-1}$ Zn and 300 to 700 $\mu\text{g}\cdot\text{g}^{-1}$ Fe) and shrimp ($>500 \mu\text{g}\cdot\text{g}^{-1}$ Zn and 200 to 500 $\mu\text{g}\cdot\text{g}^{-1}$ Fe). During monsoon, flux of metals through the estuary is increased and aquatic organisms exposed to estuarine water tend to accumulate more metals (Mitra and Chaudhury 1993b; Mitra et al. 1995). Tendency to accumulate metals in water and shrimp during monsoon was also recorded in some brackishwater ponds of Kulti region of Sunderban (Mitra et al. 1999).

We reported deposition of heavy metals in water, sediment, shrimp and fish in five such brackishwater bodies of the Sunderban during the culture period (July–September) of *P. monodon* in 1998 (Guhathakurta and Kaviraj 2000). However, deposition of heavy metals in these ponds in between *P. monodon* crops i.e. during the post–monsoon (November–December) and the pre–monsoon (April–May) is not known.

The present study was undertaken to determine: (i) the concentration of some heavy metals in the water and sediment of these brackishwater ponds during off seasons, (ii) the spatial and temporal variations in heavy metal deposition, and (iii) the correlations between heavy metal concentration and physico-chemical variables in the ponds.

Materials and Methods

Studies were made in five brackishwater ponds in different localities in the Sunderban during the period November–December 1998 and April–May 1999. We had studied heavy metal deposition in the same ponds during July–September of 1998. The locality nearest the sea (Bay of Bengal) was denoted as S1 while the farthest was denoted as S5. Localities in between

were denoted as S2, S3 and S4. A detailed description of these localities has been given earlier (Guhathakurta and Kaviraj 2000).

Two ponds were selected in each locality. Random samples of water and sediment soil were collected from each pond and mixed together to make a composite sample for each pond. Therefore, for each locality we had duplicate set of samples.

Water samples were collected from 50 cm depth in each pond. For trace metal analyzes, water was filtered through Qualigens 640d filter paper (equivalent to Whatman filter paper no. 42), acidified with HNO_3 ($1\text{ mL}\cdot\text{L}^{-1}$ of water sample). Samples were stored in neutral polyethylene bottles previously washed in acid. For determination of NO_3^- and PO_4^{3-} , filtered water was acidified with HCl ($1\text{ mL}\cdot\text{L}^{-1}$ of water sample) and stored in borosilicate glass bottles. Dissolved oxygen of water was fixed in samples collected in 100 mL reagent bottles by manganous sulfate and alkaline potassium iodide and for determination of other variables (pH, alkalinity, salinity, conductivity, ammonia and nitrite) water samples were collected in air-tight neutral polyethylene bottles. All samples of water were immediately brought to the laboratory. Water samples collected for trace metal estimation was preserved at -4°C until used for metal extraction, while physico-chemical variables of water were determined within 12-24 hours of collection.

Sediment samples were collected at random from 10 cm depth of ponds using a steel trowel. Each pooled sample was packed separately in acid-soaked clean polyethylene packets and brought to the laboratory in ice buckets. In the laboratory the sediment samples were dried at 105°C to constant weight and ground and the fraction passing a BS20 sieve was stored in clean acid-soaked polyethylene packets at -20°C .

Before analysis of metals, water samples were brought to room temperature. The sample was mixed well and 50 mL aliquot was taken in a Kjeldahl flask. 5 mL concentrated HNO_3 was added to the aliquot and the flask was gradually heated in a water bath (temperature $98\pm 2^\circ\text{C}$). The heating was continued until the solution became almost transparent and was reduced to 10 mL. Subsequently the solution was cooled, filtered under reduced pressure, diluted with deionized distilled water and was stored in acid-washed glass bottles (APHA 1995). Blanks were prepared from deionized distilled water carried through all the above procedures.

Sediment samples were also brought to room temperature and were digested with strong HNO_3 and HCl following the method of Van Loon (1980). Extracted samples were filtered under reduced pressure through acid-soaked Qualigens 640d filter paper and were stored in acid washed glass bottles.

Concentrations of metals in the filtered extracts were measured by flame atomic absorption spectrophotometry using a Varian AA-575 (air-acetylene flame). Cd was measured at wavelength 228.8 nm, Zn at 213.9 nm, Pb at 217.0 nm and Fe at 248.3 nm. Concentrations were calibrated with Johnson-Matthey standard solutions. The precision and accuracy of determination was checked by repeated analyzes of the sub samples of the standards and by recovery tests outlined by Nafde et al (1998). Adopted

analytical procedures yielded 94 to 97% recovery of the spiked metals from the samples tested. The minimum concentration of metals that could be determined (MDL) were 0.01 mg·L⁻¹ Cd and Zn, 0.02 mg L⁻¹ Pb and 2.50 mg·L⁻¹ Fe.

Physico-chemical variables of water were determined by standard methods (APHA 1995). The pH of sediment was determined with a digital electronic pH meter and conductivity with a digital direct reading conductivity meter in a 1:20 suspension of sediment sample in deionized water. Total organic carbon in the sediment was determined by the dichromate oxidation method. Available phosphate in the sediment sample was extracted with Olsen's extractant (Olsen et al. 1954) followed by Dickman and Bray's (1940) chlorostannous reduced molybdophosphoric blue color method in a hydrochloric acid system (Jackson 1967).

Statistical Analyzes

Two way ANOVA was carried out in order to determine significant variation in metal concentration in water and topsoil among the sampling stations and seasons (Gomez and Gomez 1984). Since assumptions necessary for computation of parametric statistics could not be fulfilled, correlation between metal concentration and other physicochemical variables was explored using Kendall's rank correlation coefficient τ (Das and Das 1993).

Results

The concentrations of Cd, Pb, Fe showed significant seasonal variation (Table 1). Only the Cd concentration of water varied significantly among the localities (sampling stations). Cd and Pb were consistently detected in higher concentrations in water during the post-monsoon (November-December)

Table 1. Concentration of metals (mean $\pm$ SD) in water at different seasons and localities. Values in bold type are the maximum concentrations.

		Concentrations ($\mu\text{g}\cdot\text{ml}^{-1}$)			
		[Cd] ^{1,2}	[Zn]	[Pb] ¹	[Fe] ¹
Site 1	Nov-Dec	0.019 $\pm$ 0.001	0.007 $\pm$ 0.010	0.284 $\pm$ 0.116	0.058 $\pm$ 0.004
	Apr-May	0.015 $\pm$ 0.004	<MDL	0.179 $\pm$ 0.051	8.227 $\pm$ 4.470
Site 2	Nov-Dec	<MDL	<MDL	0.361 $\pm$ 0.027	0.387 $\pm$ 0.000
	Apr-May	0.010 $\pm$ 0.013	0.057 $\pm$ 0.028	0.130 $\pm$ 0.057	1.280 $\pm$ 0.142
Site 3	Nov-Dec	0.040 $\pm$ 0.005	<MDL	0.596$\pm$0.054	0.188 $\pm$ 0.203
	Apr-May	0.019 $\pm$ 0.003	0.063 $\pm$ 0.016	0.080 $\pm$ 0.013	1.931 $\pm$ 0.035
Site 4	Nov-Dec	0.030 $\pm$ 0.007	<MDL	0.292 $\pm$ 0.054	0.762 $\pm$ 0.047
	Apr-May	0.005$\pm$0.003	0.043 $\pm$ 0.009	<MDL	1.304 $\pm$ 0.497
Site 5	Nov-Dec	0.030 $\pm$ 0.042	0.736$\pm$1.041	0.368 $\pm$ 0.305	1.492 $\pm$ 0.891
	Apr-May	<MDL	0.112 $\pm$ 0.159	0.107 $\pm$ 0.025	12.291$\pm$7.662

¹Values varied significantly among seasons ($P<0.05$)
²Values varied significantly among localities ($P<0.05$)

samplings. In contrast, Fe was detected in lower concentrations in water in all the localities during post-monsoon (November-December) than next pre-monsoon (April-May).

The concentration of all metals in the top layer of the sediment showed significant seasonal variation (Table 2). However, only Pb and Fe showed significant variation among the localities. Cd and Pb increased in concentration in the sediment from post-monsoon (November-December) to the next pre-monsoon (April-May). The reverse was found for concentration of Fe in the sediment. Seasonal variation of Zn concentration in the sediment showed different patterns in different localities.

The physico-chemical properties of water varied widely among the localities (Table 3). Pattern of seasonal differences also differed among the localities. Only total alkalinity and NO_3^- -N of water were seen to have decreased during post-monsoon in all the localities. Physico-chemical variables of sediment soil (Table 4) also varied widely among the localities and with season, with the exception of sediment conductivity. Sediment conductivity was higher during post-monsoon than the next pre-monsoon in all stations except at S5. Evaluation of Kendall's rank correlation coefficient among different variables showed perfect positive correlation of water PO_4^{3-} with pH of water ($t = 1.000$; $P < 0.05$; two-tailed) and conductivity of water with salinity of water ($t = 1.000$; $P < 0.05$; two-tailed) only during pre-monsoon. None of the physico-chemical properties were correlated with metal concentration in either of water or of sediment.

Discussion

The results presented here indicate that the metals deposited in the brackishwater ponds under study vary among seasons. Concentrations of Cd, Pb and Fe in water and sediment showed significant variations between post-monsoon and next pre-monsoon. Earlier studies made in the same

Table 2. Concentration of metals (mean $\pm$ SD) in topsoil at different seasons and localities. Values in bold type are the maximum concentrations.

		Concentrations ($\mu\text{g}\cdot\text{ml}^{-1}$)			
		[Cd] ¹	[Zn] ¹	[Pb] ^{1,2}	[Fe] ^{1,2}
Site 1	Nov-Dec	0.7 $\pm$ 0.2	30.9 $\pm$ 2.0	27.4 $\pm$ 3.1	14899.2 $\pm$ 1702.7
	Apr-May	1.8 $\pm$ 0.5	34.4 $\pm$ 0.6	54.0 $\pm$ 1.0	5859.4 $\pm$ 1723.9
Site 2	Nov-Dec	<MDL	32.5 $\pm$ 3.2	12.3 $\pm$ 16.7	11979.6 $\pm$ 180.9
	Apr-May	3.0 $\pm$ 1.8	18.6 $\pm$ 25.5	61.7 $\pm$ 2.9	6730.4 $\pm$ 1331.1
Site 3	Nov-Dec	<MDL	24.3 $\pm$ 2.7	20.9 $\pm$ 0.9	10697.9 $\pm$ 798.1
	Apr-May	1.2 $\pm$ 0.1	29.1 $\pm$ 0.6	52.3 $\pm$ 1.2	5057.9 $\pm$ 1910.2
Site 4	Nov-Dec	0.3 $\pm$ 0.5	42.7 $\pm$ 22.8	20.3 $\pm$ 3.6	19263.7 $\pm$ 70.9
	Apr-May	1.3 $\pm$ 0.1	24.1 $\pm$ 1.3	58.3 $\pm$ 4.1	6679.6 $\pm$ 2202.8
Site 5	Nov-Dec	<MDL	14.8 $\pm$ 13.1	25.6 $\pm$ 17.5	9707.1 $\pm$ 35.5
	Apr-May	1.4 $\pm$ 0.1	32.6 $\pm$ 0.6	71.4 $\pm$ 17.6	6343.5 $\pm$ 741.4

¹Values varied significantly among seasons ($P < 0.05$)

²Values varied significantly among localities ($P < 0.05$)

ponds during July-September 1998 (Guhathakurta and Kaviraj 2000) showed concentration of metals in water in the range Cd 0.04 to 0.11 $\mu\text{g}\cdot\text{mL}^{-1}$, Zn <0.01 to 9.67 $\mu\text{g}\cdot\text{mL}^{-1}$, Pb 0.03 to 0.20 $\mu\text{g}\cdot\text{mL}^{-1}$, Fe 14.4 to 175.0 $\mu\text{g}\cdot\text{mL}^{-1}$. All these metals were found concentrated in the top layer of the sediment (Cd 0.01 to 0.54 $\mu\text{g}\cdot\text{g}^{-1}$, Zn 41 to 3448 $\mu\text{g}\cdot\text{g}^{-1}$, Pb 7 to 25 $\mu\text{g}\cdot\text{g}^{-1}$, Fe 7155 to 10062 $\mu\text{g}\cdot\text{g}^{-1}$). Main source of these metals in the ponds is the drainage of metallic pollutants through Hooghly estuary. During July-September, there is heavy precipitation in the area resulting in increased drainage through the estuary. Salinity of water is also reduced during monsoon, which in turn helps pre-

Table 3. Physico-chemical properties (mean $\pm$ SD) of water in the study ponds at different seasons and localities (S1 to S5). <DL signify values under determination limits

		Dissolved Oxygen ($\text{mg}\cdot\text{L}^{-1}$)	Alkalinity ($\text{mg}\cdot\text{L}^{-1}$) as CaCO_3	Hardness ($\text{mg}\cdot\text{L}^{-1}$) as CaCO_3	Salinity (‰)	Nitrate ($\text{mg}\cdot\text{L}^{-1}$)
Site 1	Nov-Dec	2.2 $\pm$ 1.9	32.0 $\pm$ 2.8	173.0 $\pm$ 29.7	4.7 $\pm$ 0.7	0.7 $\pm$ 0.0
	Apr-May	20.9 $\pm$ 2.4	93.5 $\pm$ 0.7	315.0 $\pm$ 7.1	9.7 $\pm$ 0.1	2.7 $\pm$ 2.4
Site 2	Nov-Dec	16.0 $\pm$ 4.2	106.0 $\pm$ 14.1	5.8 $\pm$ 0.4	0.2 $\pm$ 0.1	<DL
	Apr-May	14.4 $\pm$ 1.7	134.0 $\pm$ 42.4	11.8 $\pm$ 5.37	2.3 $\pm$ 3.0	3.1 $\pm$ 1.0
Site 3	Nov-Dec	12.0 $\pm$ 0.0	67.0 $\pm$ 1.41	20.0 $\pm$ 0.0	6.5 $\pm$ 0.3	<DL
	Apr-May	8.0 $\pm$ 0.0	70.0 $\pm$ 0.0	12.0 $\pm$ 0.0	3.2 $\pm$ 0.0	2.7 $\pm$ 0.0
Site 4	Nov-Dec	13.1 $\pm$ 0.0	104.0 $\pm$ 0.0	30.0 $\pm$ 0.0	6.0 $\pm$ 0.3	<DL
	Apr-May	10.4 $\pm$ 0.0	140.0 $\pm$ 0.0	7.0 $\pm$ 0.0	1.4 $\pm$ 0.0	0.6 $\pm$ 0.0
Site 5	Nov-Dec	7.5 $\pm$ 0.7	101.0 $\pm$ 1.4	74.5 $\pm$ 0.7	1.5 $\pm$ 0.0	<DL
	Apr-May	7.2 $\pm$ 0.0	160.0 $\pm$ 0.0	74.5 $\pm$ 0.7	0.4 $\pm$ 0.0	0.6 $\pm$ 0.0
		Nitrite ($\text{mg}\cdot\text{L}^{-1}$)	Ammonia ($\text{mg}\cdot\text{L}^{-1}$)	Phosphate ($\text{mg}\cdot\text{L}^{-1}$)	pH	Conductivity (mmho)
Site 1	Nov-Dec	0.02 $\pm$ 0.02	0.16 $\pm$ 0.16	0.07 $\pm$ 0.02	7.80 $\pm$ 0.28	10.25 $\pm$ 0.07
	Apr-May	<DL	<DL	0.03 $\pm$ 0.01	7.60 $\pm$ 0.14	23.00 $\pm$ 1.41
Site 2	Nov-Dec	0.02 $\pm$ 0.01	0.07 $\pm$ 0.03	0.02 $\pm$ 0.01	6.50 $\pm$ 0.07	4.21 $\pm$ 0.16
	Apr-May	0.03 $\pm$ 0.03	0.30 $\pm$ 0.40	0.06 $\pm$ 0.01	7.78 $\pm$ 0.60	6.50 $\pm$ 8.77
Site 3	Nov-Dec	0.03 $\pm$ 0.01	<DL	0.48 $\pm$ 0.08	6.15 $\pm$ 0.07	12.40 $\pm$ 0.14
	Apr-May	<DL	0.30 $\pm$ 0.30	0.26 $\pm$ 0.14	8.35 $\pm$ 0.07	9.50 $\pm$ 0.14
Site 4	Nov-Dec	<DL	<DL	<DL	6.25 $\pm$ 0.07	9.70 $\pm$ 0.14
	Apr-May	1.10 $\pm$ 0.40	0.30 $\pm$ 0.20	<DL	7.55 $\pm$ 0.07	3.90 $\pm$ 0.14
Site 5	Nov-Dec	0.04 $\pm$ 0.02	0.13 $\pm$ 0.00	0.66 $\pm$ 0.33	8.40 $\pm$ 0.14	6.40 $\pm$ 0.14
	Apr-May	0.40 $\pm$ 0.10	0.10 $\pm$ 0.10	<DL	7.75 $\pm$ 0.07	1.45 $\pm$ 0.01

Table 4. Physico-chemical properties (mean $\pm$ SD) of sediment in the study ponds at different seasons and localities. <DL signify values under determination limits

		Mineralizable Nitrogen ($\text{kg}\cdot\text{ha}^{-1}$)	Organic Carbon (%)	pH	Conductivity (mmho)	Soil Phosphate (ppm)
Site 1	Nov-Dec	42.3 $\pm$ 0.4	0.3 $\pm$ 0.2	8.4 $\pm$ 0.1	0.8 $\pm$ 0.0	92.3 $\pm$ 42.0
	Apr-May	40.8 $\pm$ 0.4	<DL	8.5 $\pm$ 0.1	0.2 $\pm$ 0.0	111.6 $\pm$ 7.9
Site 2	Nov-Dec	65.9 $\pm$ 4.4	1.0 $\pm$ 0.0	8.3 $\pm$ 0.1	0.2 $\pm$ 0.0	162.9 $\pm$ 36.5
	Apr-May	40.8 $\pm$ 0.4	<DL	8.7 $\pm$ 0.1	0.1 $\pm$ 0.0	117.3 $\pm$ 13.3
Site 3	Nov-Dec	50.2 $\pm$ 4.4	1.1 $\pm$ 0.0	8.0 $\pm$ 0.1	0.6 $\pm$ 0.0	135.4 $\pm$ 33.2
	Apr-May	29.8 $\pm$ 0.4	0.5 $\pm$ 0.0	8.1 $\pm$ 0.1	0.3 $\pm$ 0.0	168.1 $\pm$ 23.5
Site 4	Nov-Dec	36.1 $\pm$ 0.4	0.3 $\pm$ 0.0	5.1 $\pm$ 0.1	1.0 $\pm$ 0.0	186.5 $\pm$ 0.1
	Apr-May	50.2 $\pm$ 0.4	1.2 $\pm$ 0.0	6.7 $\pm$ 0.1	0.4 $\pm$ 0.0	239.1 $\pm$ 18.5
Site 5	Nov-Dec	112.9 $\pm$ 4.4	0.8 $\pm$ 0.0	7.4 $\pm$ 0.1	0.5 $\pm$ 0.0	160.1 $\pm$ 14.8
	Apr-May	70.6 $\pm$ 0.4	0.8 $\pm$ 0.0	8.7 $\pm$ 0.1	0.7 $\pm$ 0.0	134.8 $\pm$ 24.7

precipitated metals to dissolve, thereby increasing the availability of metal ions in water (Lakshmanan and Nambisan 1983). During November-December (post-monsoon) the drainage is reduced resulting in reduction of heavy metal influx to the ponds. Concentrations of Zn and Fe in water, as observed in the present investigation, are also considerably reduced as compared to July-September (Guhathakurta and Kaviraj 2000). Concentration of Cd is also reduced, but concentration of Pb in water is considerably increased in November-December as compared to July-September. During April-May (next pre-monsoon) precipitation is little and drainage is further reduced. As a result, in most of the sites concentration of the metals, except Fe, are reduced in water and increased in the sediments. Fe concentration, on the contrary, is reduced in the sediments and increased in water during April-May as compared to November-December.

Increase in concentration of metals in water during monsoon and deposition of the metals from water into sediment of the pond after monsoon is quite natural. But results of the present study indicate that Pb is retained in pond water even after monsoon and deposition pattern of Fe from water to sediment is reversed during the post-monsoon period to next pre-monsoon as compared to other metals. Heavy drainage during monsoon transports silts and clay particles into the ponds. There is evidence that clay minerals exhibit selective affinity for Pb^{2+} over Zn^{2+} ions (Mitchell 1964). Thus if clay particles remain suspended in water for long it may adsorb Pb preferentially over other metals. When such clay particles are precipitated (during April-May), Pb is also deposited over sediment. In the sediment also Pb may be adsorbed preferentially over Zn^{2+} resulting in desorption of Zn already adsorbed (Förstner 1983). Results of the present study revealed that concentration of Pb increased in the pond sediment during April-May as compared to November-December in all the sites and concentration of Pb in each site was higher than that of Zn during April-May. During this period concentration of Zn increased in the pond water in sites 2, 3 and 4.

However, there is wide difference of Zn concentration, both in water and sediment, of the ponds between July-September (Guhathakurta and Kaviraj 2000) and November-December (present study). High concentration of Zn in water during July-September coincides with huge flux of the metal during monsoon (Mitra et al. 1999). During November-December, the flux of metals is reduced thereby reducing the concentration of Zn in water. However, sediment of brackishwater ponds in Sunderban continuously change due to deposition of silts carried through tidal waters of the estuary. Top layer (0 to 10 cm) of the pond sediment studied in the present investigation (November-December) probably originated from fresh deposition and did not reflect the metal concentration determined in the sediment during July-September.

Pattern of seasonal fluctuation of Fe in water and sediment is different from that of Cd and Pb. We observed high concentrations of phosphate both in sediment and water and NO_3^- in water during April-May. The PO_4^{3-} and NO_3^- form complexes with Fe and could cause remobilization of the metal from sediment (Samanidou and Fytianos 1990). However, we could not

correlate concentration of metals in water or sediment with any of the physico-chemical variables evaluated. Previously we had estimated metals partitioned into different chemical compartments of the sediment of these brackishwater ponds through sequential leaching procedure of Tessier et al. (1979). It was observed that most of the Fe was bound to mineral lattices of the sediment leaving only a little portion loosely bound (Guhathakurta and Kaviraj 2000). Anthropogenic flux of metals is reflected only in the fractions of metals that are loosely bound. Mobility of metals in between sediment and aqueous phase also depends upon these fractions of metals. Therefore, it is difficult to explain seasonal fluctuations of Fe in the sediment of brackishwater ponds of Sunderban on the basis of total metal concentration.

A wide and significant variation in Pb and Fe concentrations was found for sediment among the localities (Table 2). Highest and lowest concentrations detected in the sediment were Pb, 71.4 (S5) and 12.3 (S2) $\mu\text{g}\cdot\text{g}^{-1}$, and Fe 19263 (S4) and 5859 (S1) $\mu\text{g}\cdot\text{g}^{-1}$, respectively. Such a difference among the localities may be due to difference in the quantity of drainage among the localities or differential enrichment of the metals resulting from vertical migration from deeper strata. Both Fe and Pb are relatively immobile and largely retained in the soil (Borg and Johansson 1989) in contrast to Zn and Cd, which can migrate within the sediment and bring about enrichment in the surficial sediments (Berner 1980). Thus, spatial variations of Fe and Pb in the sediment is probably due to the difference in drainage pattern in different localities.

Depending upon provisional maximum tolerable daily intake (PMTDI) of metals for humans (Cd 1 $\mu\text{g}\cdot\text{g}^{-1}$; Zn 1000 $\mu\text{g}\cdot\text{g}^{-1}$; Pb 3.5 $\mu\text{g}\cdot\text{g}^{-1}$; Fe 800 $\mu\text{g}\cdot\text{g}^{-1}$) World Health Organization (WHO) has set the guideline value for most of these metals (Cd-0.003 $\mu\text{g}\cdot\text{mL}^{-1}$; Pb- 0.005 $\mu\text{g}\cdot\text{mL}^{-1}$; Fe- 2.0 $\mu\text{g}\cdot\text{mL}^{-1}$) in drinking water (WHO 1996). Drinking water usually makes a negligible contribution to Zn intake in human unless very high concentration of the metal occurs in water. Results of the present study indicate that in the ponds under study, concentrations of Cd, Pb and Fe in water often exceed the WHO guideline values of these metals for drinking purpose. However, these pond waters are not generally used for drinking purpose. But the metals present in these waters are capable to bio-concentrate in fish and shrimps cultured in these waters and humans consuming such fish or shrimp may exceed the PMTDI levels of these metals. Deb and Santra (1997) observed, in a sewage fed fish pond ecosystem, that from a relatively innocuous concentration of Pb (0.09 $\mu\text{g}\cdot\text{mL}^{-1}$) and Zn (0.23 $\mu\text{g}\cdot\text{mL}^{-1}$) in water fish could concentrate 78 to 80% higher amount of Pb and 77% higher amount of Zn in their body. In brackishwater ponds of Sunderban shrimps have been found to accumulate Zn at much higher level than fish (Ghosal et al. 1997). Possibilities of bioaccumulation of metals in shrimp and subsequent health hazards are hardly considered before the start of shrimp culture particularly in traditional bheris of Sunderban. It is revealed from the present study that heavy metal concentrations in water of these bheris are lower during pre-monsoon as compared to monsoon period but are still unsafe to start hazardless shrimp culture.

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