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Heavy Metal Concentration in Pore Water of Salt Marsh along the Karnafully River Coast, Bangladesh

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ABSTRACT

Heavy metal concentrations (Fe, Cu, Zn, Cd and Pb) in salt marsh pore water of Karnafully River coast were investigated in this study. Water samples of four different locations were analyzed for selected heavy metals by AAS (Atomic Absorption Spectrophotometry). The mean values of heavy metals were recorded 4.63±2.035 μg mL^{-1} for Fe, 0.32±0.080 μg mL^{-1} for Cu, 0.66±0.319 μg mL^{-1} for Zn, 0.03±0.008 μg mL^{-1} for Cd and 0.25±0.085 μg mL^{-1} for Pb in this study. It is also observed that Cd is found to positively correlate with NO_2-N ($r = 0.957$, $p<0.05$) and Zn ($r = 0.970$, $p<0.05$). However, positive correlations were also found between Cu and Fe ($r = 0.985$, $p<0.05$) and Cu and Zn ($r = 0.959$, $p<0.05$) in salt marsh pore water. The mean concentration of Fe, Cd and Pb were found above the recommended value which may indicate a fresh and continuous contamination of salt marsh pore water due to anthropogenic activities.

Key words: Heavy metals, pore water, Karnafully River coast, Bangladesh

INTRODUCTION

Among all the aquatic ecosystems, salt marshes are the most productive ecosystems in the planet as it acts as a buffer zone between terrestrial and aquatic ecosystems (Rajendran *et al.*, 1993). In the estuarine environment, continuous interactions between freshwater and salt water systems lead to influence the heavy metal transportation into estuarine water, soil, plants and aquatic organisms (Ip *et al.*, 2006). Generally, in aquatic ecosystem, metals occur in low concentrations and they are neither created nor destroyed by human (Authman and Abbas, 2007; Ndimele and Jimoh, 2011). Salt marshes act as protective filters and repositories for runoff pollutants (Teal and Howes, 2000), pathogens (Grant *et al.*, 2001) and different types of nutrient (Howes *et al.*, 1996; Weis and Weis, 2003).

Different pollutants from domestic and industrial effluents can be easily stabilized and immobilized in the salt marsh water and sediments. These heavy loads of pollutants are responsible for the availability of heavy metals in the salt marsh environment (Azmat *et al.*, 2007; Stolz and Oremland, 1999). Banu (1995) demonstrated that heavy metals can partly be retained and accumulated (Gambrell, 1994; Williams *et al.*, 1994) in the salt marsh sediment. In Porteresia bed, water-soluble metals and exchangeable metals are the most available and precipitated inorganic compounds, metals complexes with large molecular weight, humus materials and metals adsorbed to hydrous oxides are also possibly available (Gambrell, 1994; Williams *et al.*, 1994). But metals precipitated as insoluble sulfide form and some metals bound with minerals are essentially unavailable in salt marsh pore water and sediments (Gambrell, 1994).

Though Bangladesh is a small country, around 230 rivers including 53 international rivers flow across this country. Fresh water plays an important role in agricultural purposes and industrial process (BCAS, 2000). Urbanization and industrialization on the river bank is an important factor for the continuous contamination of water bodies (Doe, 2001; Kakar *et al.*, 2006). Several studies (Doe, 2001; Hossain, 2001) showed that surface water quality of the rivers of the country is highly polluting day by day.

Karnafully is the most important river of Chittagong that falls into the Bay of Bengal. Thousands of the industries and factories are situated on the bank of the Karnafully River or very close to the river system and they don't have any waste treatment facilities (Das *et al.*, 2002). They discharge the untreated waste into the nearest water bodies which finally reach into Karnafully River through different canal system. Every year, thousands of ships and oil tankers come at Chittagong port to carry goods and fuel (Khan and Khan, 2003; Das *et al.*, 2002). As a result, various refuse and disposable materials are being discharged and oil spills from the ships (Ogbo and Okhuoya, 2011), oil tankers and fishing boats get mixed with the water and sediments of Karnafully River.

The presence and contamination of heavy metals in the estuarine environment is of major concern due to their heavy toxicity and bio-accumulating tendency. Pollution by heavy metals is a threat to human life and the total environment as well as the wetland ecosystem (Igwe and Abia, 2006; Islam and Tanaka, 2004). However, the structure and functioning of salt marshes are subjected to many human activities in coastal and estuarine areas. Heavy metals are an important class of pollutant in the aquatic environment. Some heavy metals such as Mercury, Lead, Cadmium, Copper and Zinc have been shown in some previous investigations to occur at a significant level in the salt marsh pore water and sediments. The accumulation of these heavy metals might affect the coastal ecosystems as well as salt marsh biota.

In view of the economic importance of the coastal regions and the adverse effects of metal pollution on living resources, the present study was carried out to investigate the concentration of Heavy metals like Pb, Cd, Zn, Cu and Fe in the salt marsh pore water along the Karnafully River coast, Bangladesh.

MATERIALS AND METHODS

Study site: Karnafully is the most important river of Chittagong. Karnafully river is originated from the Lushai Hills of Assam in India at Latitude 22°54' N and Longitude 92°27' E (O' Mallery, 1908) and then enters the districts of Chittagong from the north eastern side. The total length of the Karnafully River is about 170 miles and empties into the Bay of Bengal (Mahmood *et al.*, 1976). Four stations selected for the sampling were Station-1 (Rajukhali khal, Location: 22°19.67' N and 91°51.13' E), Station-2 (Chaktai khal, Location: 22°19.55' N and 91°50.49' E), Station-3 (Monowerkhali khal, Location: 22°19.48' N and 91°49.98' E) and Station-4 (Chittagong Port, Location: 22°18.48' N and 91°48.63' E) (Fig. 1).

Sample collection: Water samples were collected during Monsoon season (June-August), 2010 from the study area of the littoral zone using a glass bottle. The samples were preserved in cleaned glass jars and transferred to the laboratory for the analysis. Water samples for dissolved metal analysis were collected separately with Van Dorn water sampler and stored in a 1 L polyethylene bottle with 5 mL HNO_3.

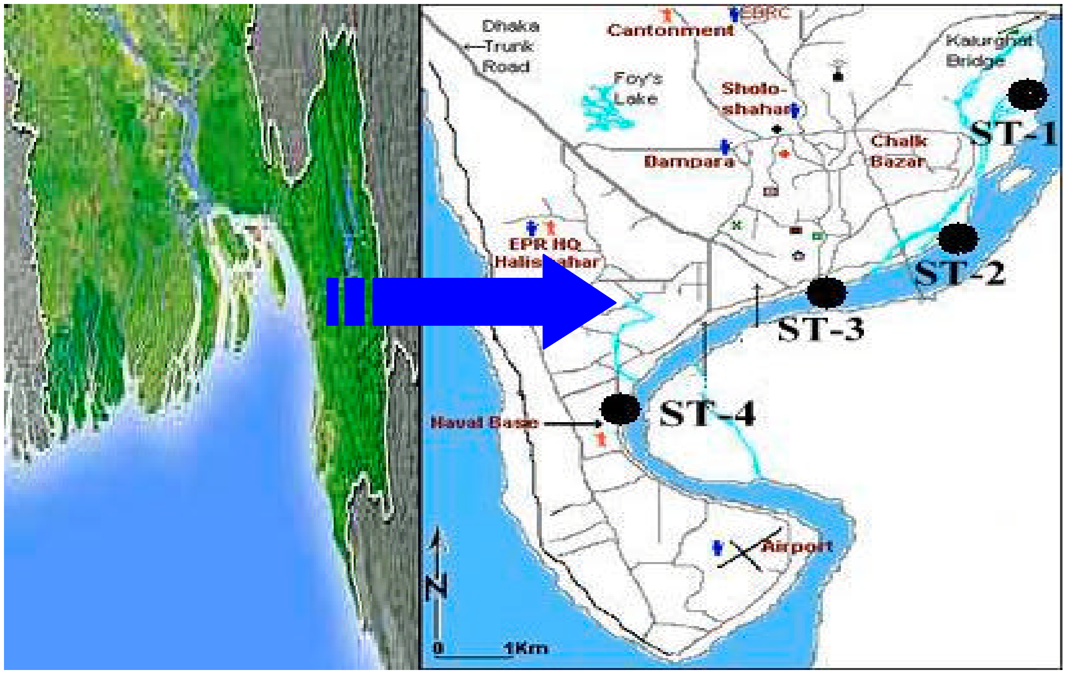

Fig. 1: Study area showing sampling locations

Determination of sulphate, nitrate and phosphate in water samples: Sulphate, nitrate and phosphate were determined using standard procedure (Standard methods, 1976; DWAF, 1992). Nitrate as N was determined by the cadmium reduction metal method, while the concentration of phosphate in the samples were determined using the ascorbic acid method by reacting in with adding reagent containing molybdate and an acid to give a blue coloured complex.

Digestion of samples for the assessment of heavy metal concentrations: Two hundred and fifty milliliter of well mixed acidified water samples were kept in Pyrex Backer and evaporated the samples on water bath (temperature above 100°C) placing watch glass on each beaker to about dryness. Five milliliter concentrated HNO_3 was added in each beaker and digested on water bath and filtered by a filter paper (Quantitative Whatman 541) and was made the filtrate to 25 mL with de-ionized water in a 25 mL volumetric flask. Blank digestion was carried out for each sample.

Atomic absorption spectrophotometric measurement: All determination were made using a Perkin-Elmer 3110 Atomic Absorption Spectrophotometer (AAS) with an air acetylene flame and hollow cathode single and combination lamps as light source for the metals under test were used in this work. The following wave lengths were used to run: Cd 228.8, Cu 324.8, Zn 213.9, Pb 283.3 and Fe 248.3.

Statistical analysis: The correlation of nutrients and concentrations of heavy metals in salt marsh pore water were assessed using Pearson's correlation analysis. All the statistical analyses of the collected data were performed by using Statistical software SPSS 19.0. Statistical significance was tested at 95% confidence level.

RESULTS AND DISCUSSION

Beside the heavy metals (Fe, Cu, Zn, Cd and Pb), some nutrients like PO_4-P, NO_2-N and SiO_3-Si have been determined in this study. The concentrations of nutrients and heavy metals are not uniform at all the selected sampling locations. Maximum concentrations of PO_4-P, NO_2-N and SiO_3-Si were recorded 64.302±13.07 (Station 2), 14.285±5.04 (Station 2) and 1826.677±382.07 (Station 1), respectively. Minimum concentrations of PO_4-P, NO_2-N and SiO_3-Si were found 50.523±8.62 (Station 1), 6.349±1.55 (Station 4) and 1128.242±208.74 (Station 3), respectively. The mean concentrations of PO_4-P, NO_2-N and SiO_3-Si are presented in Table 1.

The maximum concentrations (μg mL^{-1}) of Fe, Cu Zn, Cd and Pb were recorded as 7.66±1.67 (Station 2), 0.43±0.10 (Station 2), 1.08±0.17 (Station 2), 0.04±0.04 (Station 2) and 0.34±0.08 (Station 3), respectively. The minimum concentrations (μg mL^{-1}) of Fe, Cu Zn, Cd and Pb were found to be 3.30±0.40 (Station 1), 0.26±0.07 (Station 4), 0.32±0.12 (Station 4), 0.02±0.02 (Station 4) and 0.14±0.06 (Station 1), respectively. Figure 2 is represented the comparison of the mean concentration and standard deviation of heavy metals (Fe, Cu, Zn, Cd and Pb) among the sampling locations.

The present study showed that salt marsh pore water contain higher amount PO_4-P, NO_2-N and SiO_3-Si. The mean concentration of PO_4-P and NO_2-N obtained from this is found at a higher level than the results found by Mahre *et al.* (2007). The results also indicate that the concentration of Cd, Pb and Fe exceed the aforesaid recommended values while concentrations of Cu and Zn were lower than the recommended value. Higher concentration of heavy metals might be due to huge discharge of domestic and industrial effluents, oil and wastage of ship and fishing vehicles and other anthropogenic activities. A number of studies suggested that Fe has frequently been used as an indication of natural changes in the heavy metals carrying capacity of the water (Rule, 1986). The mean concentration of Fe was found above the recommended level (2.37±0.37 μg mL^{-1}) in the salt marsh pore water. Das *et al.* (2002) worked on Karnafully River estuary, recorded concentrations of Fe in water samples ranged between 20.025-42.203 μg mL^{-1} which is much higher than the findings of the present study (4.63±2.035 μg mL^{-1}).

It has been argued that Cu is closely related to the aerobic degradation of organic matter (Das and Nolting, 1993) as most marine organisms have developed their mechanisms to regulate concentrations of Cu in their tissues in the presence of variable concentrations in the surrounding water, pore waters and food (Neff, 2002). Zn is one of the earliest known heavy metals and has been argued that a large amount of Zn entering the oceans of the world is derived from aerial deposition (Neff, 2002). The mean concentrations of Cu (0.32±0.080 μg mL^{-1}) and Zn (0.66±0.319 μg mL^{-1}) are below than the recommended value. The maximum concentrations of Cu and Zn are less than the finding of Das *et al.* (2002) and Banu (1995). The mean concentration of Cd and Pb of present study is slightly higher (Cd = 0.03±0.008 μg mL^{-1} and Pb = 0.25±0.085 μg mL^{-1}) than the recommended value but these findings are less than the previous investigations on Karnafully River estuary by Das *et al.* (2002). The higher concentration

Table 1: Nutrients and heavy metal concentrations in salt marsh pore water of Karnafully River coast (Values in μg mL^{-1})

Station	PO_4-P	NO_2-N	SiO_3-Si	Fe	Cu	Zn	Cd	Pb
1	50.523±8.62	10.714±2.11	1826.677±382.07	3.30±0.40	0.26±0.13	0.54±0.48	0.03±0.02	0.14±0.06
2	64.302±13.07	14.285±5.04	1181.968±642.55	7.66±1.67	0.43±0.10	1.08±0.17	0.04±0.04	0.28±0.07
3	59.709±4.50	8.531±3.00	1128.242±208.74	4.17±0.29	0.32±0.09	0.68±0.18	0.03±0.01	0.34±0.08
4	55.116±7.91	6.349±1.55	1322.355±428.97	3.41±0.30	0.26±0.07	0.32±0.12	0.02±0.02	0.23±0.05

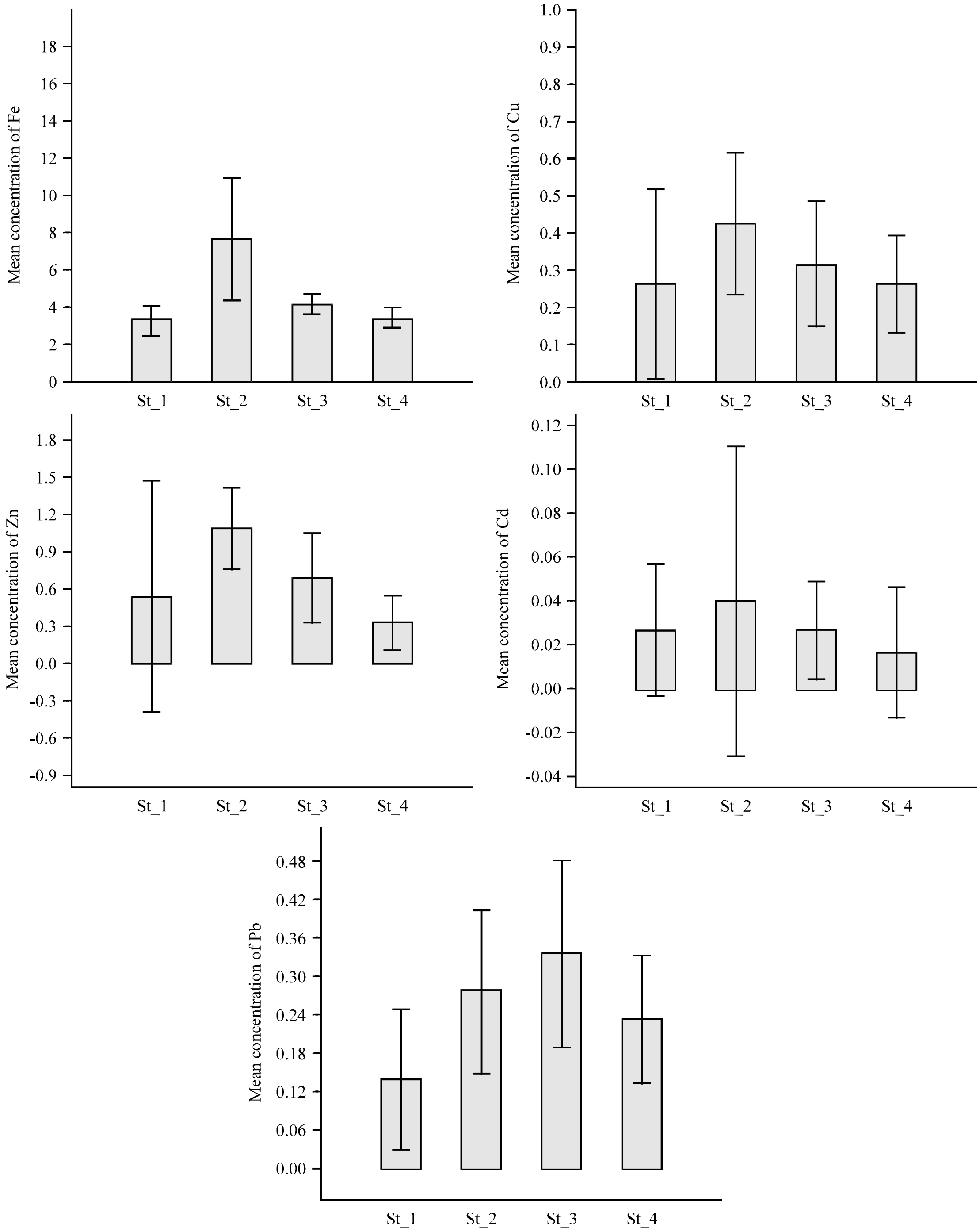

Fig. 2: Comparison of the mean concentration and standard deviation of heavy metals (Fe, Cu, Zn, Cd and Pb) among the sampling locations

of Cd and Pb in the pore water might be due to the untreated industrial effluents and oil spill from the ship and oil tankers of Chittagong port. Table 2 is presented the comparison of detected values of heavy metals with recommended values of unpolluted water and previous investigations on estuarine water.

Table 2: Comparison of detected values of heavy metals with recommended values of unpolluted water and previous investigations (Values in μg mL^{-1})

Metal	This study (μg mL^{-1})	Recommendation value (μg mL^{-1})	Previous investigation (μg mL^{-1})
Fe	4.63±2.035	2.370±0.37	20.025-42.203 (Das *et al.*, 2002)
Cu	0.32±0.080	1.620±0.11	0.372-0.918 (Das *et al.*, 2002)
Zn	0.66±0.319	1.100±0.14	0.472-1.186 (Das *et al.*, 2002)
Cd	0.03±0.008	0.019±0.002	0.090-0.217 (Das *et al.*, 2002)
Pb	0.25±0.085	0.027±0.005	0.405-1.195 (Das *et al.*, 2002)

Table 3: Pearson correlations among the nutrients and heavy metal elements in salt marsh pore water of Karnafully River coast

	PO_4-P	NO_2-N	SiO_3-Si	Fe	Cu	Zn	Cd	Pb
PO_4-P	-							
NO_2-N	0.492	-						
SiO_3-Si	-0.862	0.015	-					
Fe	0.870	0.823	-0.513	-				
Cu	0.918	0.795	-0.591	0.985*	-			
Zn	0.799	0.901	-0.401	0.933	0.959*	-		
Cd	0.632	0.957*	-0.180	0.845	0.866	0.970*	-	
Pb	0.809	-0.011	-0.949	0.423	0.544	0.423	0.241	-

*Correlation is significant at the 0.05 level

To compare with recommended values of unpolluted seawater and previous investigations, it is observed that the mean concentration of Fe, Cd and Pb found in this study were relatively higher. However, the mean concentrations of most of the heavy metals were found at lower amount than that of previous studies at different locations of Karnafully River estuary. The first reason is that the sampling locations were different and secondly, the previous study was investigated on Karnafully River water. The mean concentration of heavy metals might differ at pore water of soil from the river water as they are stabilized and precipitated into salt marsh sediments.

In the correlation matrix among the nutrients and the heavy metal elements, Cd is found to positively correlate with NO2-N ($r = 0.957$, $p<0.05$) and Zn ($r = 0.970$, $p<0.05$). However, positive correlation were also found between Cu and Fe ($r = 0.985$, $p<0.05$) and Cu and Zn ($r = 0.959$, $p<0.05$) in salt marsh pore water. The correlation matrix of the nutrients and heavy metal elements in salt marsh pore water of Karnafully River coast is presented in Table 3.

CONCLUSION

Generally the land base activities, domestic and industrial wastage and ship waiting at the port are the main source of heavy metals in the study area. The results of present study reveal that Cd, Pb and Fe exceeded the recommended values and provided little indication of metal pollution which did not reach the alarming condition. Nevertheless, if this trend of contamination continues, it may seriously affect on this salt marsh ecosystem along the Karnafully River coast.

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