Bioavailability of trace metals in sediment cores from sunderban mangrove wetland, india: An urgent need for bioremediation

Santosh Kumar Sarkar[A] and Bhaskardeb Bhattacharya[A]

[A] Department of Marine Science, University of Calcutta, 35 B.C.Road, Calcutta, India, Email sarkar.santosh@gmail.com

Abstract
The paper attempts to identify the enrichment pattern of acid leachable trace metals (ALTMs) such as Fe, Mn, Cr, Cu, Ni, Pb, Cd, Co, Ag and As and their relationship with sediment quality parameters (pH, organic carbon and texture) in core sediments (<63µm particle size) from Indian Sunderban mangrove wetland, India. The results indicate that the change in pH values causes coagulation and precipitation of ALTMs. Fe and Mn have fairly close distribution patterns of enrichment in surface layers which might be ascribed to early diagnetic processes. The most prominent feature of ALTMs is the enrichment of Fe, Mn, Cr, Cu, Ni and Pb in the surface-subsurface layers in the sediment cores, which is mainly attributed to the intense industrial and agricultural activities as well as drainage of domestic sewage to this coastal region. The ALTMs also indicate their association with organic carbon and Fe-Mn oxyhydroxides. The enrichment is well- supported by the correlation, grouping and clustering of ALTMs in statistical analyses. Anthropogenic Factor (AF) values indicated ALTMs enrichment for all heavy metals due to intense anthropogenic activities. The result suggests the urgent need for phytoremediation using mangrove plants as remediation strategy to decontaminate the sediments contaminated with inorganic contaminants.

Key Words
Acid leachable, phytoremediation, enrichment, Indian Sunderban

Introduction
Sediments are the important component of ecosystem in which toxic compounds accumulate through complex physical and chemical adsorption mechanisms depending on the properties of the adsorbed compounds and the nature of the sediment matrix (Leivouri, 1998). The leaching of metals provides an accurate measure of the bioavailable metals in any aquatic environment which are often readily available to organisms affecting them directly. Hence assessment of trace metal enrichment in sediments on the acid leachable (non-residual) elements is of prime interest, as it often yields more data on the extent of trace metal enrichment than the total sediments, which include the residual or non-residual fraction, and so may mark the relationships sought.

Methods
Selection of Sampling sites, collection of samples and preservation
The Indian Sunderban ($21^0$31'6" to $22^0$12' 14" N and $88^0$11' 28"to $89^0$05'53" E), formed at the estuarine phase of the Hugli river of an area of ~ 9600 km^2, is a mangrove wetland belonging to the low-lying coastal zone. Six sampling sites were selected, namely, Lot 8 (S_1), Gangasagar (S_2), Jharkhali (S_3), Gosaba (S_4), Canning (S_5) and Dhamakhali (S_6). The sites have diverse human interferences with a variable degree of exposure to heavy metal and trace organic contamination. Core samples were collected from the six selected sites with the help of a steel corer (40 cm in length and 5 cm in diameter) which is gently pushed into the sediments and retrieved back in sealed position. They were transported in frozen conditions (- 4° C) to the laboratory. The samples were oven dried (40° C) and were disaggregated using an agate mortar and pestle, sieved through 63µm sieve, which was stored in pre-cleaned inert polypropylene bags for further chemical analyses.

Analytical methods
The extraction of acid leachable metals was done by weighing 5 g of dry sediment sample in a 100 ml plastic bottle in which 75 ml of 0.5 N HCl was added and after mechanically shaking for 16 h it was filtered with Whatman 'A' filter paper. The final filtered solution was analyzed for ALTMs in ICP-MS. High purity standards (NIST, USA) were used and standard solutions were prepared. The accuracy of the analysis was determined by standard addition method and the recovery of elements was 75-97%. A standard reference material MAG1 was used to ensure the quality control and accuracy of the analysis. All statistical analyses were carried out by the software package STATISTICA 6.0.

Results

Regarding textural composition, the four stations (S_1 to S_4) show variable admixture of sand, silt and clay with an overall size range from sandy to clayey very fine. This wide array of textural differences may be attributed to vigorous estuarine mixing, suspension-resuspension and flocculation-deflocculation processes. The pH values of core samples are mainly basic in nature (pH from 8.1 to 8.9). Organic carbon (OC) values are very low (0.18% - 3.52 %) which might be due to the mixing processes and marine sedimentation at the sediment water interface, where the rate of delivery, as well as the rate of degradation by microbial-mediated processes, can be high (eg. Canuel and Martens, 1993). Fe and Mn have fairly close distribution patterns of enrichment in surface/subsurface layers (~0-8 cm) in sediment cores (Fe: 3937-5201 mg kg^{-1}; Mn: 300-615 mg kg^{-1}) at all the stations (excepting S_2 and S_5) which might be due to the early diagnetic processes as well as the strong association to the geochemical matrix between the two elements. The distribution pattern of seven ALTMs (Cr, Cu, Ni, Pb, Ag and As) exhibits variations between sites and depths in the core samples which is ascribed to the metal deposition in mangrove sediments through natural processes as well as anthropogenic activities. Peak values of Cu, Ni, Pb, Ag and As in Dhamakhali (S_3) (at 32-36 cm depth) indicate scavenging of trace metals by Fe and Mn oxyhydroxides and are deposited as metal sulphides with a common source of (Prohic and Kniewald, 1987. Distribution of Cr concentrations in the sediment core indicates higher values in top layers (0-8 cm) at all six sites which suggest that it is present as Cr (VI), which is readily adsorbed by Fe and Mn oxides (Davis *et al*., 1996), is relatively mobile and after release in the pore waters, they migrate downward into the reducing zone and precipitates again as Cr $(OH)_2$ (Shaw *et al*., 1990). Vertical profiles of Cu indicate the relatively high acid-leachable values in the top layer in (S_1) (31.5 to 48.6 mg/kg), (S_4) (36.7 to 51.6 mg/kg) and (S_6) (48.9 to 69.8 mg/kg). This is due to the presence of humic-copper complexes and indicates the presence of anthropogenic input under reducing conditions . Like Cu, a similar trend of enrichment of Ni was also observed in the top layer (0-8 cm) at same three sites. This indicates that it is also due to the presence of a mobile fraction of these metals in sediments successively bound to humic acids in the mangrove sediments. Profiles of Pb in the surface layers (0-8 cm) show relatively higher concentrations at Canning (S_6) (19.6 to 21.2 mg/kg) than Jharkhali (S_4) (16.5 to 17.3 mg/kg) and are attributed to the local redox conditions, which allowed Pb to be co-precipitated with Mn during Mn-oxide formation in the surficial sediment. Likewise, the levels of Cd, Ag do not vary greatly in the core profiles of all the six stations which might be due to homogenous input of this metal in the wetland system. The sources of As stem from anthropogenic activities like intense exploitation of ground water, application of fertilizers and insecticides as well as burning of coal for domestic purposes. The concentration of As and Cu exceeded the Effects-Range Low (ER-L) values of (8.2 and 34 µg/g respectively, Long *et al*., 1995) indicating that there may be some ecotoxicological risk to the benthic organisms. The cluster diagram based on the linear pair coefficient pair of correlation between different variables of six different core samples forms two different clusters (as shown in Fig. 1) : elemental association with sand and organic carbon (cluster I) and association with mud, carbonate and pH (cluster II). The association of Ni, Pb, Cu, Mo, Ba, As (contaminant elements) in cluster I clearly suggests that they have a common origin in the aquatic environment. The higher values of anthropogenic factors (AFs) (>1) in all the core samples indicate that the area is affected by the heavy input of industrial effluents from the industries situated in the upstream side of the feeding rivers in the mangrove region.

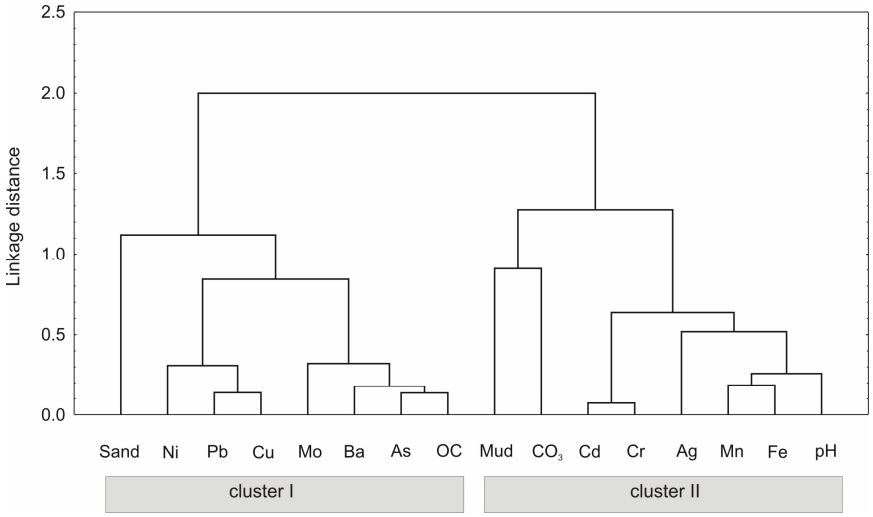

Figure 1. Results of cluster analysis based on complete linkage method for core samples in Sunderban wetland.

Conclusion

The work presents comprehensive data base of ALTMs in core sediments of Sunderban mangrove wetland highlighting the geochemical processes concerned with the differences in distribution patterns. The results indicate that ALTMs are trapped in the mangrove sediments due to the change in pH conditions at various sites and the reduction of organic carbon and carbonates in the mangrove region. The down core profile distribution of ALTMs also suggests that Fe, Mn enrichment is due to the diagnetic behaviour of the metal. The authors strongly recommend phytoremediation as potential strategy using mangrove plants as excluder species for nonessential metals and regulators of essential metals.

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