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Accumulation of Trace Metals by Mangrove Plants in Indian Sundarban Wetland: Prospects for Phytoremediation

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The work investigates on the potential of ten mangrove species for absorption, accumulation and partitioning of trace metal(loid)s in individual plant tissues (leaves, bark and root/pneumatophore) at two study sites of Indian Sundarban Wetland. The metal(loid) concentration in host sediments and their geochemical characteristics were also considered. Mangrove sediments showed unique potential in many- fold increase for most metal(loid)s than plant tissues due to their inherent physicochemical properties. The ranges of concentration of trace metal(loid)s for As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn in plant tissue were 0.006–0.31, 0.02–2.97, 0.10–4.80, 0.13–6.49, 4.46–48.30, 9.2–938.1, 0.02–0.13, 9.8–1726, 11–5.41, 0.04–7.64, 3.81–52.20 $\mu\text{g g}^{-1}$ respectively. The bio-concentration factor (BCF) showed its maximum value (15.5) in *Excoecaria agallocha* for Cd, suggesting that it can be considered as a high-efficient plant for heavy metal bioaccumulation. Among all metals, Cd and Zn were highly bioaccumulated in *E. agallocha* (2.97 and 52.2 $\mu\text{g g}^{-1}$ respectively). Our findings suggest that the species may be classified as efficient metal trap for Cd in aerial parts, as indicated by higher metal accumulation in the leaves combined with BCF and translocation factor (TF) values.

Keywords geochemical characteristics, *Excoecaria agallocha*, bioaccumulation

Introduction

Mangroves are facultative halophytes and form a unique group of intertidal ecosystems. They are increasingly threatened due to anthropogenic chemicals sourced from uncontrolled agricultural runoff, urban and industrial effluents and wastewaters, coupled with urbanization and population growth. Despite being exposed to metal contaminated sediments, mangroves seem to be highly tolerant to heavy metals. This may be due to the ability of mangroves to exclude or regulate uptake of metals at root level and limit translocation to the shoot (MacFarlane and Burchett 2001). Mangrove sediments are anaerobic and reduced, as well as rich in sulphide and organic matter. They

therefore favor the retention of water-borne trace metals (Tam and Wong 2000) and the subsequent oxidation of sulphides allows metal mobilization and bioavailability (Clark *et al.* 1998).

The present study has been undertaken with the following objectives: (i) to investigate the extent of accumulation and the distribution of trace metal(loid)s in individual plant tissues (ii) to establish correlation between metal(oids) present in sediments and plant tissues and (iii) to find out the suitable candidate for phytoremediation species to be used for conservation and sustainable management of Sundarban coastal regions.

Materials and Methods

Area of Investigation

The Indian Sundarban, formed at the estuarine phase of the Hugli (Ganges) River Estuary is a tide-dominated mangrove wetland belonging to the low-lying humid and tropical coastal

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zone. This vulnerable environment suffers from environmental degradation due to rapid human settlement, tourism and port activities, and operation of excessive number of mechanized boats, deforestation and increasing agricultural and aquaculture practices. A significant ecological change is pronounced in this area due to reclamation of land, deforestation, huge discharges of untreated or semi-treated domestic and municipal wastes and effluents from multifarious industries such as tanneries, chemicals, paper and pulp, pharmaceuticals as well as contaminated mud disposal from harbor dredging. All these factors impart a variable degree of anthropogenic stresses leading to elevated concentrations of heavy metals.

Two study sites, Chandanpiri (S_1) and Jharkhali (S_2) have been chosen for the present investigation, covering the eastern and western flank of Sundarban (Fig. 1). The later (S_2) is more diversely populated with mangrove species ($n = 7$) than the former (S_1) ($n = 4$) and this anomalous distribution patterns of mangrove species is related to multiple factors, such as influence of environmental gradients (especially salinity), wave energy and tidal amplitude controlling sediment dispersal patterns.

Collection and Processing of Sediment Samples

Sediment samples were collected in triplicate from top 0–5 cm of the surface at each sampling site (Corsolini *et al.* 2012) over an area of 1m x 1m using a clean, acid-washed plastic scoop. Samples were stored in clean plastic zip lock pouches and transported to the laboratory. Individual sediment samples were placed in a ventilated oven at low temperature (max. 45°C) (Watts *et al.* 2013) as high temperature may contribute to the alteration of volatile and even non-volatile organics of the sample (Mudroch and Azcue 1995), until they get completely dried. Samples were pulverized using an agate mortar and pestle, sieved through 63 μm metallic mesh since this fraction contains more sorbed metal per gram of sediment due to its larger specific surface area (Chatterjee *et al.* 2009) and individually transferred into pre-cleaned, inert polypropylene bags and stored at room temperature until subsequent extraction and chemical analyses. Sediment pH was determined by pH meter (Water Analyzer 371). Organic carbon (C_{org}) content of the sediments was determined following a rapid titration method (Walkey and Black, 1934). Mechanical analyses of substrate sediments were done by sieving in a Ro-Tap shaker (Krumbein and Pettijohn 1938), and statistical computation of textural parameters was done by using the formulae of Folk and Ward (1957) and following standards of Friedman and Sanders (1978).

Collection and Preservation of Mangrove Samples

During October – November (2012), plant organs of *Avicennia officinalis*, *A. marina*, *A. alba* (Avicenniaceae), *Bruguiera gymnorrhiza*, *Ceriops tagal*, *Rhizophora apiculata* (Rhizophoraceae), *Aericeros corniculatum* (Myrsinaceae), *Excoecaria agallocha* (Euphorbiaceae), *Lumitzera racemosa* (Combretaceae), *Heritiera fomes* (Malvaceae), *Sonneratia*

caseolaris (Lythraceae) were randomly collected, from different trees belonging to the same species at low tide conditions for root / pneumatophore collection in tidal exposure.

For analyses of plant samples, we took leaves of two different stages of development: young and mature as well as trunk bark, pneumatophores/roots in consideration. Sample organs were collected from trees that were greater than 1m tall with a girth at breast height of greater than 2 cm and that were of similar health conditions (as determined by degree of predation on leaves) and were then sampled with a thin stainless steel knife. Samples were thoroughly washed by deionised water in the laboratory to remove dust, sediment particles and algal trace. These were oven-dried under 50°C until they became completely dried and then homogenized (methods adapted by MacFarlane *et al.* 2003). Samples were preserved in clean sealed plastic zip pouches for further analyses.

Analytical Protocol

The dried sediment samples were prepared by microwave digestion (Multiwave 3000, Anton Paar) with aqua regia in closed Teflon vessels (Walsh *et al.* 1997). The determination of total metal(loid) contents was performed using current analytical methods, including: Atomic Absorption Spectrometry (AAS, SOLAAR M Series equipment from Thermo–Umicam) for Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn; coupled graphite furnace AAS for As and Cd; and a hydride generation system (HGS) linked to an atomic absorption for Hg. Most of the trace metal(loid)s in consideration were very low in concentration in the samples, so precautions were taken and necessary instruments were used for particular trace metal(loid)s.

The plant samples were also microwave digested with an $\text{HNO}_3\text{--H}_2\text{O}_2$ mixture in closed Teflon vessels, which was followed by analysis with AAS for Cu, Fe, Mn and Zn; coupled graphite furnace AAS for As, Cd, Co, Cr, Ni and Pb due to the reduced sample amount and to increase sensitivity; and a hydride generation system (HGS) linked to an atomic absorption for Hg (Fletcher 1981; Brooks 1983; Van Loon 1985).

The detection limits for metal(loid)s in sediment samples were 0.004 $\mu\text{g g}^{-1}$ for Cd; 0.01 $\mu\text{g g}^{-1}$ for As and Hg; 0.4 $\mu\text{g g}^{-1}$ for Zn; 1 $\mu\text{g g}^{-1}$ for Co, Cu, Mn and Ni, 1.5 $\mu\text{g g}^{-1}$ for Cr and Pb; 2 $\mu\text{g g}^{-1}$ for Fe. The detection limits for metal(loid)s in plant samples were 0.002 $\mu\text{g g}^{-1}$ for Cd; 0.005 $\mu\text{g g}^{-1}$ for As, Hg and Pb; 0.01 $\mu\text{g g}^{-1}$ for Cr and Ni; 0.02 $\mu\text{g g}^{-1}$ for Co; 0.5 $\mu\text{g g}^{-1}$ for Cu and Mn; 0.8 $\mu\text{g g}^{-1}$ for Fe; 0.2 $\mu\text{g g}^{-1}$ for Zn.

Quality assurance and quality control

Certified reference material for sediment (2711 SRM reference material Montana Soil, from LGC Promochem, Barcelona, Spain), and for plant materials (Virginia Tobacco Leaves (CTA-VTL-2, Poland), were used to ensure the quality control and accuracy of the analyses. The agreement between the certified reference values and the values determined by the analytical method were in the range of 87.8% to 108.2%.

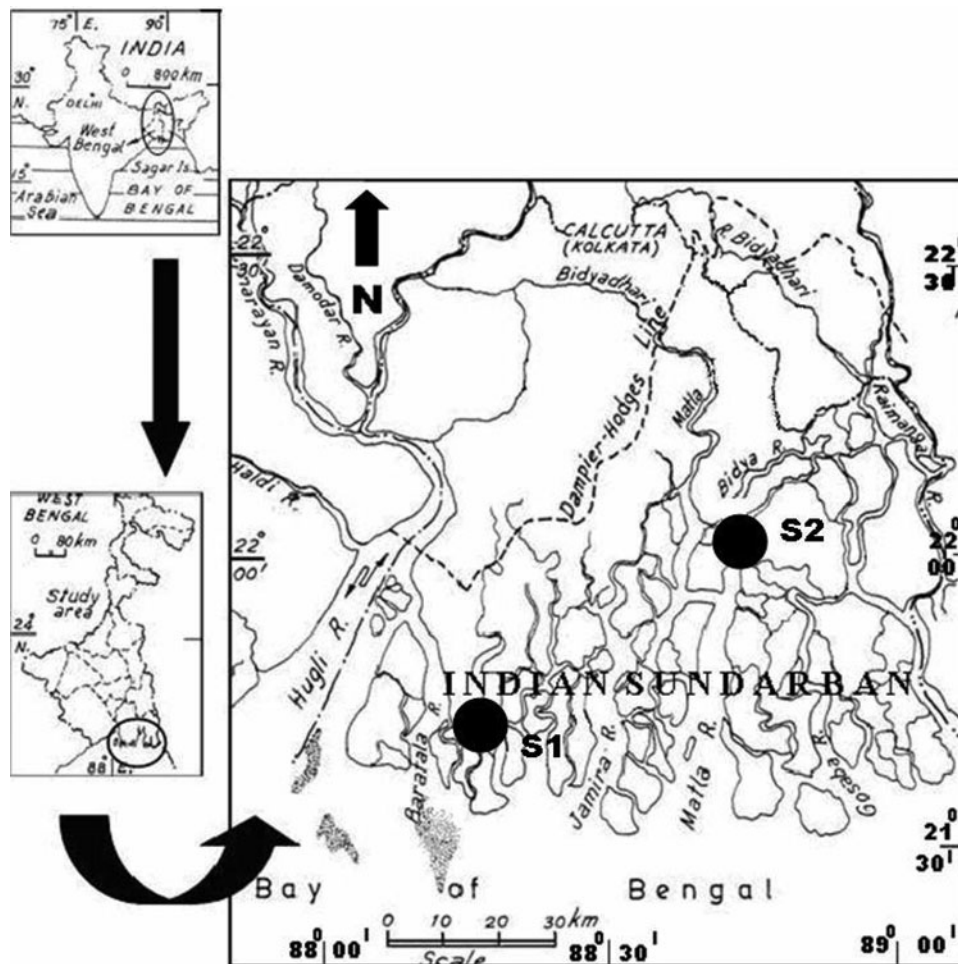


Fig. 1. Map showing location of two study sites Chandanpiri (S_1) and Jharkhali (S_2) in Indian Sundarban wetland.

Concentration and Translocation Factors

In order to compare the degree of storage of the metal(loid)s, bio-concentration factors (BCF) were calculated as concentration of metal(loid) in tissue over the concentration of metal(loid) in sediment. Translocation factor (TF) was described as ratio of trace metal(loid)s in plant shoot to that in plant root (Usman and Mohamed 2009; Usman *et al.* 2012). It is important to note that $TF > 1$ indicates that the plant translocates metals effectively from root to the shoot (Baker and Brooks 1989).

Statistical Analyses

Partitioning of individual metal(loid)s in plant tissues and sediments were pooled over site and sampling time and analyzed using one-way ANOVA in the ANOVA module of STATISTICA Statsoft Inc. 1995. Statistica for windows release 5.0. Tulsa, Oklahoma, USA. It was assessed by using MINITAB 13. Weightage of independent variables was assessed by standardized beta coefficients (Statsoft Inc. 1995. Statistica for windows release 5.0. Tulsa, Oklahoma, USA). Independent variables examined with exponential accumulation relationships were log transformed $\ln(x + 1)$, prior to all calculation (Zar 1966).

Results and Discussion

Sediment Geochemistry

Sediment showed differences in their physicochemical properties pertaining to pH, C_{org} and textural properties. Values of pH are characterized by mild alkaline in nature (7.76–8.01) and were similar between plants within the same location ($p > 0.05$). According to Middleburg *et al.* (1996) mangrove sediments have basic pH values due to the limited buffer capacity of these sediments. The C_{org} values showed very low concentrations (0.60–0.66%), which might be the result of marine sedimentation and mixing processes at the sediment-water interface where the rate of delivery as well as the rates of degradation by microbial-mediated processes can be high (Canuel and Martens 1993). Regarding texture, sediment samples exhibit a variable admixture of sand (1.80–15.45%), silt (32.58–38.93%) and clay (51.98–59.28%). A variable amount of erosion and depositions in study sites can explain the observed heterogeneity in textural contents.

Possible sediment enrichment of metal(loid)s was evaluated in terms of the geoaccumulation Index (I_{geo}) of Müller (1979). It consists of seven classes. Class 0 (practically unpolluted): $I_{geo} \leq 0$; Class 1 (unpolluted to moderately polluted): $0 < I_{geo} < 1$;

Table 1. Pooled values of mean, standard deviation, median and range of 11 metals in mangrove organs and sediments of 2 study sites of Indian Sundarban

ORGANS	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
YOUNG LEAF (n = 12)											
mean	0.05	0.4	1.19	1.19	13.39	106.8	0.06	206.21	1.55	1.32	21.88
SD	±0.04	±0.27	±1.45	±0.9	±4.425	±138.2	±0.04	±197.22	±1.59	±1.5	±9.746
median	0.05	0.43	0.43	1.06	14.31	65.54	0.04	157.28	1.05	0.93	19.74
max	0.12	0.88	4.8	2.88	22.46	534	0.13	695.82	5.41	5.25	48.42
min	0.01	0.04	0.13	0.13	6.354	9.189	0.02	23.596	0.11	0.07	9.433
MATURE LEAF (n = 12)											
mean	0.1	0.37	0.65	1.15	12.44	91.66	0.06	357.76	1.38	1.65	21.16
SD	±0.08	±0.19	±0.88	±0.88	±5.981	±42.34	±0.03	±516.99	±0.93	±1.75	±10.07
median	0.07	0.4	0.18	0.68	10.61	78.68	0.04	176.96	1.31	1.04	17.92
max	0.31	0.64	2.61	2.67	28.92	168.3	0.12	1726	3.01	6.12	43.17
min	0.03	0.04	0.11	0.25	4.457	32.59	0.02	21.611	0.13	0.12	8.567
BARK (n = 12)											
mean	0.04	0.62	1.17	1.83	12.98	332.9	0.05	138.17	1.28	2.32	17.51
SD	±0.03	±0.81	±1.2	±1.17	±4.725	±221.3	±0.03	±131.44	±1.11	±2.51	±11.89
median	0.04	0.35	0.79	1.37	11.25	289.1	0.04	76.755	1.05	1.22	14.7
max	0.1	2.97	3.43	3.81	20.57	741.7	0.11	458.28	3.74	7.09	52.2
min	0.01	0.04	0.14	0.5	6.207	98.61	0.02	18.401	0.16	0.04	7.53
ROOT/PNEUMATOPHORE (n = 10)											
mean	0.06	0.18	1.02	2.17	16.3	406.5	0.06	194.98	1.59	2.78	15.51
SD	±0.04	±0.2	±1.22	±1.64	±6.76	±237.9	±0.02	±338.82	±1.06	±2.32	±5.442
median	0.05	0.09	0.51	1.72	14.59	297.3	0.06	57.853	1.48	2.28	17.07
max	0.18	0.66	3.97	6.49	31.63	938.1	0.09	1120	3.03	7.64	23.05
min	0.03	0.04	0.1	0.39	9.43	214.9	0.03	21.433	0.27	0.04	7.231
SEDIMENT (n = 6)											
mean	3.82	0.21	7.67	28.3	38.29	2942	0.07	647.25	34.5	15.8	34.42
SD	±0.84	±0.02	±1.25	±1.06	±4.61	±108.8	±0.01	±1.7227	±0.17	±5.95	±2.697
median	3.82	0.21	7.67	28.3	38.29	2942	0.07	647.25	34.5	15.8	34.42
max	4.41	0.22	8.55	29	41.55	3019	0.07	648.47	34.6	20	36.33
min	3.22	0.19	6.79	27.5	35.03	2865	0.06	646.04	34.4	11.6	32.51

Class 2 (moderately polluted): $1 < I_{geo} < 2$; Class 3 (moderately to heavily polluted): $2 < I_{geo} < 3$; Class 4 (heavily polluted): $3 < I_{geo} < 4$; Class 5 (heavily to extremely polluted): $4 < I_{geo} < 5$; Class 6 (extremely polluted): $I_{geo} > 5$ (Müller, 1979). It is calculated as follows: $I_{geo} = \log_2 [Cn/(1.5 \cdot Bn)]$, where Cn = measured content of metal "n", Bn = the metal's content in "average shale" (Turekian and Wedephol 1961) and 1.5 is the background matrix correction in factor due to lithogenic effects (Praveena et al. 2007).

The I_{geo} values showed very high values except Cd and Hg (Table 2) indicating that sediments are strongly polluted, whereas concentrations of two toxic metals, Cd and Hg, seem to have no pollution effect at two sampling sites, similar to

previous observation reported by Chatterjee et al. (2009, 2012) from the core sediments in Sundarban coastal regions.

Trace Metals in Mangrove Sediments

Mangrove sediments are anaerobic and reduced, as well as being rich in sulphide and organic matter – favouring the retention of water-borne trace metals (Silva et al. 1990; Tam and Wong 2000). However, high metal concentrations in sediments as evident from Table 1 are not reflected in mangrove plants tissues (excepting Cd and Hg). Suggested mechanisms for reduced bioavailability of metals in sediments are precipitation as sulphides under anaerobic conditions, organic

Table 2. Values of Geochemical Index (I_{geo}) and Enrichment Factor (EF) in host sediments at two study sites (S_1 and S_2)

	Study Sites	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
I_{geo}	Chandanpiri	4.80	-4.70	6.76	10.77	10.04	26.43	-5.87	18.48	10.61	7.27	11.01
	Jharkhali	5.26	-4.48	6.43	10.69	10.28	26.50	-5.66	18.49	10.62	8.06	11.17
EF	Chandanpiri	4.08	10.56	7.42	5.32	12.82	1.00	2.62	12.50	8.33	9.53	5.64
	Jharkhali	5.31	11.71	5.59	4.79	14.44	1.00	2.89	11.90	7.96	15.63	5.98

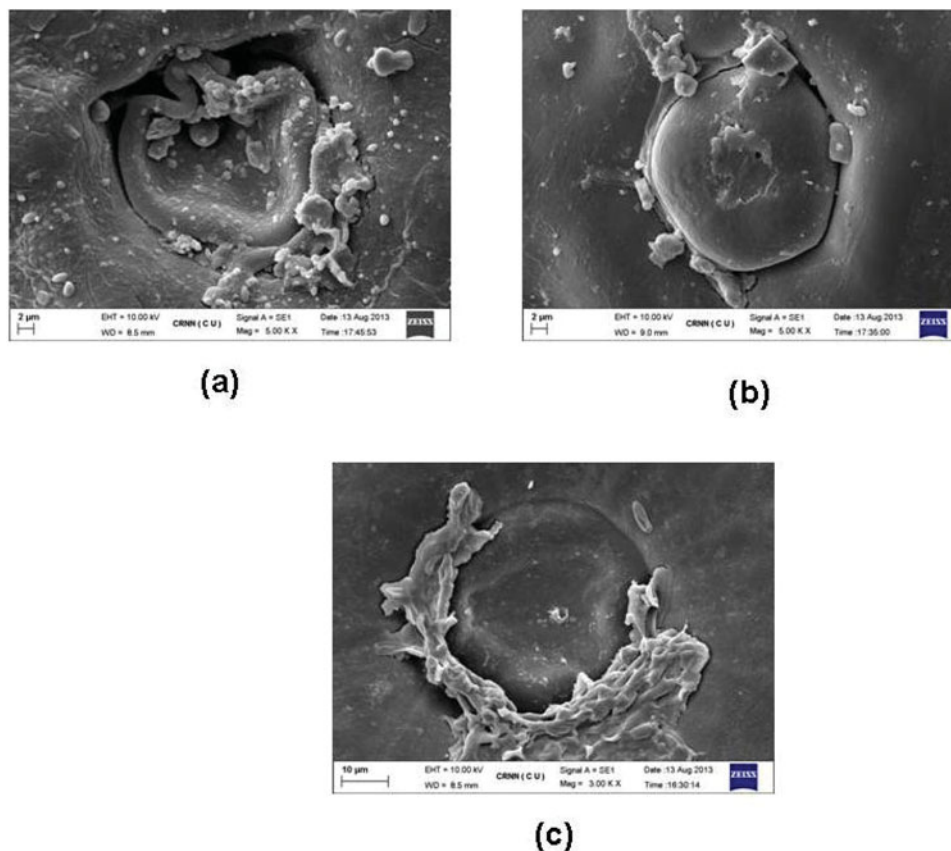


Fig. 2. Salt glands on the upper surface of leaves of (a) *Avicennia. Alba* (Magnification 5000 X, bar = 2 μm), (b) *Avicennia. officinalis* (Magnification 5000 X, bar = 2 μm), *Aegiceros. corniculatum* (Magnification 3000 X, bar = 10 μm) with excreted salt crystals.

complexation, fine sediments and Fe plaques on root surfaces (De Lacerda *et al.* 1993). Possible physiological mechanisms responsible for restricted uptake and translocation within plants include cell wall immobilization, complexation with substances such as phytochelatins and barriers at the root endodermis (Baker and Walker 1990).

The pooled mean value of trace metals in mangrove sediments of two study are summarized in Table 1 which revealed the following trend : Fe > Mn > Cu > Cr > Pb > Cd > Hg. Sediment concentrations of Zn, Cu, Ni and Pb were found to be significantly different between monitored sites over the mangrove area, excepting Fe, Mn and Cr. The observed variations may be attributed to effects of biological and physical phenomena, such as tidal inundation, salinity changes, wind and waves. These phenomena allow the processes of bioturbation, re-suspension and erosion that are known to affect the metal concentrations in surface sediments (Bellucci *et al.* 2002).

Potential Risk Assessment

Comparing our data with Effects Range Low (ERL) and Effect Range Medium (ERM) values (Long *et al.* 1995), majority of the trace metals (except Cu, Ni and Hg) showed lower concentrations than ERL. This can be related with almost no contamination level of the metals in the studied sites. Copper, Ni and Hg exhibited values lower than ERM. The site

Jharkhali (S_2), which is a tourist spot, is exposed to anthropogenic pressure primarily caused by riverine traffic. The lack of standard norms and strict regulation about fuel being used in mechanized boats for ferrying and fishing throughout the year lead to deposition of metals. On the other hand, batteries, thermometer, electric switch manufacturing industries located in the upstream of the Hugli estuary together with extensive use of antifouling paints by the local coastal people act as a potential source of metals at the site Chandanpiri (S_1).

Metal(loid)s Concentration in Mangrove Plants

The results of this study indicated that the extent of heavy metal accumulation differed among the heavy metal type and the organs of mangrove species (Table 1). An overall enrichment of the trace metal follows this sequence: Mn > Fe > Zn > Cu > Pb > Cr > Ni > Co > Cd > As > Hg. The highest concentrations of Mn and Fe in mangroves are associated with the highest concentrations in the surrounding sediments. Manganese combined with other elements is widely distributed in the Earth's crust. Manganese is essential to plant growth and is involved in the reduction of nitrates in green plants. In our study Mn showed a wide range of variation (from 18.40 $\mu\text{g g}^{-1}$ in bark of *L. racemosa* at S_2 to 1726.00 mg kg^{-1} at in mature leaf of *S. caseolaris* at S_2). Wide range of variations (from 9.20 mg kg^{-1} at in young leaf of *R. apiculata* at S_2 to

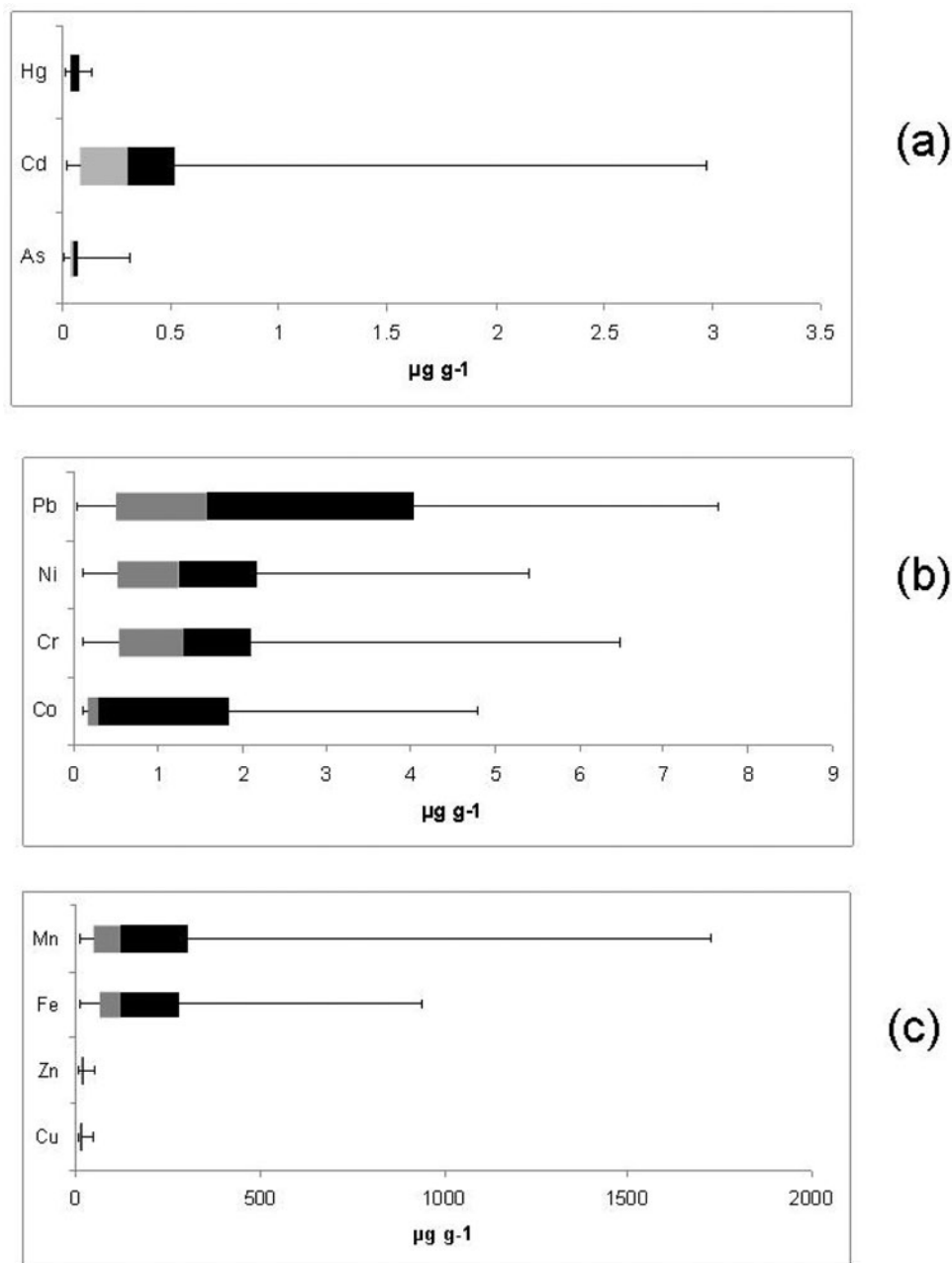


Fig. 3. Box-Whisker plots of metal concentration found in mangrove organs. All the boxes show the 25th percentile and the 75th percentile, and the whiskers represent the lowest and the highest coefficients, while the line inside the boxes expresses the median.

938.1 $\mu\text{g g}^{-1}$ in root of *C. tagal* at S_2) of Fe was observed which may be related to the precipitation of iron as iron sulphides which are common in mangrove sediments due to anoxic condition. Iron is generally described as the principal metal that precipitates with sulphide compounds in anaerobic sediments (Lynch *et al.* 2014) and these sulphides form a major sink for many metals in the mangrove area. High values are observed in mangrove systems and these high concentrations may be due to the non-anthropogenic sources such as weathering of rocks from the up streams of Hugli river and high organic resources from mangrove litter and leaves. Zn showed also relatively higher concentrations than other elements. The high concen-

trations of Cu and Zn could be explained by the fact that the set of metals are essential trace elements for plants required in chloroplast reactions, enzyme systems, protein synthesis, growth hormones and carbohydrate metabolism (Shaw 1990). They may share similar absorption mechanism (Qiu *et al.* 2011), and thus exhibited some restricted mobility, though an obvious barrier to acropetal translocation was in operation (MacFarlane *et al.* 2003). Our findings show that Cu and Zn have the moderate accumulation, whereas Pb showed limited uptake and minimal mobility suggesting presence of a strong exclusion mechanism. Indeed, Pb is very immobile and has a low solubility at $\text{pH} > 5$. Soluble Pb can react with

phosphates, hydroxides, carbonates, and clays, organic matter, which result in reducing soil Pb solubility and subsequently its availability to plants (Usman *et al.* 2013). Higher values of Pb were recorded in leaves ($6.12 \mu\text{g g}^{-1}$ at Jharkhali) and roots ($7.64 \mu\text{g g}^{-1}$ at Chandanpiri) and were within the normal range [(5.0–10.0 $\mu\text{g g}^{-1}$ of plant materials reported by Alloway (1995) and Bowen (1979)]. The sources are mainly concerned from atmospheric Pb due to vehicle exhausts from nearby major roads as well as dry cell batteries used and disposed by the local people. However elevated concentration of non-essential metals in tissues suggests a possible function of sequestering toxic metals, especially with respect to Pb (Ong Che 1999). The present result suggests the role of mangrove plants in extracting heavy metals from contaminated sites might be dependent on sediment metal availability.

The toxic elements (Hg, Cd, Cr, Co, Ni, Pb and As) showed anomalous distribution in different organs of the mangrove species as follows : Hg = $0.082 \mu\text{g g}^{-1}$ in *C. tagal* mature leaves at Jharkhali; Pb = $7.64 \mu\text{g g}^{-1}$ in *A. corniculatum* pneumatophore at Chandanpiri; Cd = $2.97 \mu\text{g g}^{-1}$ in *E. agallocha* bark at Chandanpiri; As = $0.31 \mu\text{g g}^{-1}$ in *A. officinalis* mature leaf at Jharkhali; Cr = $6.49 \mu\text{g g}^{-1}$ in *B. gymnorrhiza* root at Chandanpiri; Co = $4.8 \mu\text{g g}^{-1}$ in *A. officinalis* young leaf at Chandanpiri; Ni = $5.41 \mu\text{g g}^{-1}$ in *L. racemosa* young leaf at Jharkhali. In majority of the cases the toxic metals were found to be accumulated in leaves which may be attributed to acropetal movement of metals through translocation with the development of leaves from young to old. Several of literature indicates that many mangrove species tend to concentrate trace metals in the leaves and other vegetative parts without adverse effects on the plant (Kotmire and Bhosale 1979).

Plants have a range of different mechanisms for protecting themselves against the uptake of toxic elements and for restricting their transport within the plant (Almeida *et al.* 2006). These mechanisms include the sub-cellular compartmentalization of the metal, namely in vacuoles, and the sequestration of the metal by specially produced organic compounds, like phytochelatins, concentrating metal in the plants roots (Ross and Kaye 1994). This is also influenced by the metabolic requirements for essential micronutrients (e.g., Cu, Zn) while non-essential metal (e.g., Cd) tends to be excluded or compartmentalized (Baker and Walker 1990). For example, differences in uptake of Cd, Cr, Cu, Fe in five tissues (young and mature leaf, bark, stem and pneumatophore) of *A. corniculatum* was between 5 and 28-fold whereas Cd, Co, Mn, Pb, Cr in five tissues of *A. officinalis* was between 7 and 48-fold. Furthermore, concentrations for the same trace metal and tissue can differ within a population of the same species and between different species. Interspecific differences have been commonly reported and attributed to differences in physiology (Agoramoorthy *et al.* 2008) including the ability to excrete metals such as Zn from glandular trichomes (MacFarlane and Burchett 1999). Different translocation rates between plant organs may also act as a causative factor (Ong Che 1999). Differences in accumulation between 10 species for the same tissue and trace metal(loid) were 3- 17 fold for Cr, Ni and Hg and 5- 49 fold for As, Co, Cd and Pb whereas Cu, Fe, Mn and Zn exhibited an overall similar pattern of accumulation.

Majority of the metals showed a common trend of accumulation either in root /pneumatophore [Cr $6.49 \mu\text{g g}^{-1}$ in root of *B. gymnorrhiza*, Pb $7.64 \mu\text{g g}^{-1}$ in pneumatophore of *A. corniculatum* (both at S₁); Fe $938.10 \mu\text{g g}^{-1}$ in root of *C. tagal* (at S₂)] or bark (Cd = $2.97 \mu\text{g g}^{-1}$ and Zn = $52.20 \mu\text{g g}^{-1}$, at S₁, both in bark of *E. agallocha*). Thus these two organs act as a barrier for metal translocation and protect the sensitive aerial parts of the plants from metal contamination (Pahalawattaarachchi *et al.* 2009).

Most of the studied metals showed similar trend of accumulation either in root / pneumatophore (Cr, Cu, Fe and Mn) or in bark (Cd, Co, Fe, Pb and Zn).

Young leaves of salt excreting type showed greater accumulation capacity of some metals such as Mn ($295.3 \mu\text{g g}^{-1}$ in *A. corniculatum*), and Co ($0.25 \mu\text{g g}^{-1}$ in *A. officinalis*) than other organs which is directly related with their higher rates of secretion at the same external salinity due to the presence of salt glands (Clough 2013), as shown in Figure 2 a, b, and c. Salt secretors generally show greater ion mobility and translocation (Lawton *et al.* 1981).

Bio-concentration and Translocation Factors

The ability of plants to absorb contaminant from sediment can be expressed by the bio-concentration factor (BCF), which indicates the rate of metal content in tissue to that in sediment (Usman *et al.* 2012; Qiu *et al.* 2011). From the obtained data, the BCF values of As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn in leaf are as follows: 0.001–0.09, 0.10–15.46, 0.01–0.56, 0.005–0.22 0.13–1.38, 0.003–0.31, 0.23–2.02, 0.02–2.66, 0.003–0.16, 0.002–0.66 and 0.12– 1.61 respectively. BCF of Cd seemed to be very high (15.46) and was found in *E. agallocha*. BCF values of Cd and Zn suggest that these two metals were highly bioaccumulated in *E. agallocha* and have a greater mobility than other investigated metals. The low BCF values of Fe (0.31) and Mn (2.66) in highly metal enriched sediments (3019.00 and 648.5 mg Kg⁻¹ respectively) at S₂ can be explained by avoiding metal uptake by mangroves and/ or by low bioavailability of metals in sediments. The ability of phytoextraction capacity has also been expressed by a translocation factor (TF), which is defined as the ratio of the metal concentration in the leaf to that in the roots (Usman *et al.* 2012). Generally, plant species with TF values 16.1 are classified as high-efficient plants for metal translocation from the roots to above ground parts of plants. Therefore, our findings suggest that *E. agallocha* may be classified as potential accumulator for Cd and Zn, as indicated by higher metal concentrations in barks (2.97 and 52.2 mg kg^{-1}).

Statistical Analyses

From the correlation matrix results of it is revealed that the metalloid As is significantly correlated with the metals like Cr, Fe and Ni, suggesting the similar sources and deposition mechanism in case of all organs at both sampling sites. Cobalt with Cu and Cr showed significant positive correlations in all cases at Jharkhali (S₂) and in young leaves at Chandanpiri. Arsenic also exhibited the similar trend of correlation with

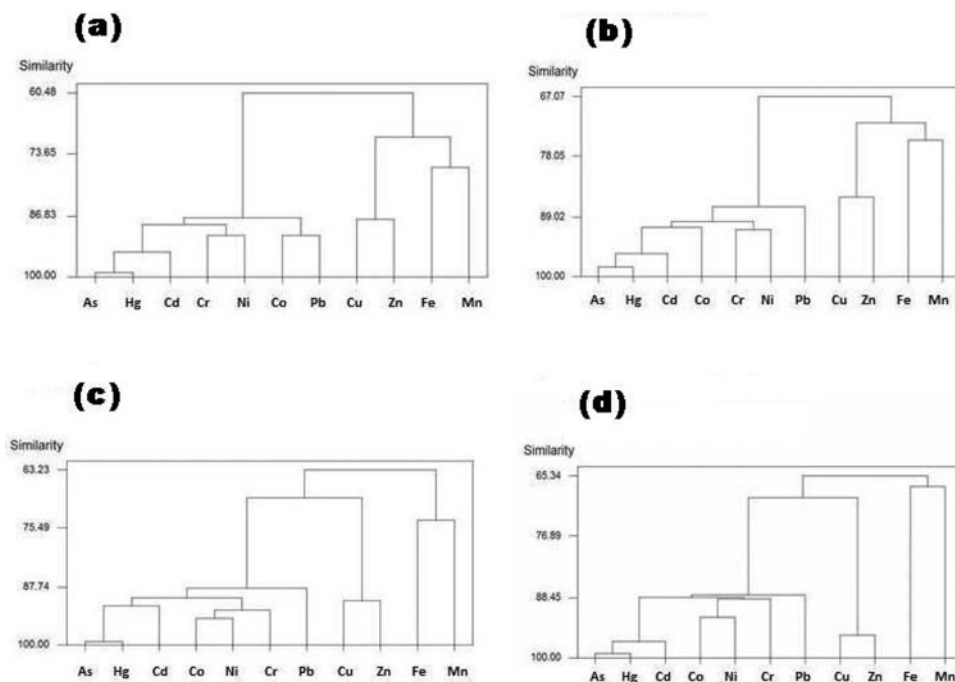


Fig. 4. Dendrogram showing the relationship between metals in different mangrove organs: (a) young leaf, (b) mature leaf, (c) bark and (d) root/pneumatophore) both study sites (Chandanpiri and Jharkhali).

Pb, Nickel showed positive significant correlation with Cr except pneumatophores at Jharkhali. From the result of one way ANOVA it is revealed that all mangrove plants showed significant differences between metal concentrations in study sites ($df = 10$; $F = 472.22$; $p < 0.01$) at 1% significance level.

The results of discriminant analysis, when used in conjunction with the Box-and-whisker plots, provided statistical evidence that the trace metals were not homogeneously distributed in all mangrove organs as shown in Figure 3. Concerning the differences observed among the metals considered, the present study demonstrates that both Fe and Mn have unique potential to get accumulated in plant tissues in the Sundarban environment, which may have occurred as both the elements are essential for plant growth and development and is required as a cofactor for proteins that are involved in a number of important metabolic processes including photosynthesis and respiration (Morgan and Connolly 2013).

For all mangrove plant organs a similar pattern of clustering between As- Hg, Cu- Zn, Fe-Mn was recorded as revealed in Figure 4 a, b, c, d. Mangroves may share similar absorption and exclusion mechanisms for toxic elements like As and Hg. Cadmium, being a toxic element, is present in the 1st outliers for all four plant organs and indicates similar mechanisms of absorption/elimination processes up to certain extent. In young and mature leaves, Cr- Ni clustered together and indicates same exclusion mechanism for them through defoliation. In bark and root tissues, Co- Ni clustered together with Cr in 1st outliers indicating restricted mobility of them within the plant body. Cu- Zn which are essential micronutrients and Fe - Mn which have similar sources shared similar absorption mechanisms. In sediments too, clustering of Fe- Mn as

well as the toxic metal (loid)s Cd- Hg and As- Co were also evident.

Conclusions

The study has demonstrated the efficiency for trace metal accumulation in mangrove plants of tropical Sundarban wetland by adopting complex and cohesive adaptive strategies. These include sediment-plant interactions, modifications of anatomical structure of the plant organs as well as intracellular binding mechanisms. This is evident that the coastal halophytes could act as the potential buffer corridor against waterways pollution for essential and toxic trace metal(loid)s and thus could be used as a suitable tool for biogeochemical barriers to the transit of heavy metal(loid)s. The present study indicates that mangrove species *E. agallocha* can be considered as the most promising candidate for phytoremediation and ecological restoration as it could tolerate and accumulate a range of trace metals. This plant based, low cost technology for the removal of the toxic contaminants could be extensively used for estuarine management to protect Sundarban coastal regions for the removal of toxic pollutants.

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