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Comparative study of heavy metals in selected mangroves of Sundarban ecosystem, India

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Abstract

Accumulation and partitioning of eight heavy metals Cr, Pb, Zn, Cd, Ni, Cu, Co and Fe were studied in the root, stem and leaf of mangrove species (*Sonneratia caseolaris*, *Acanthus ilicifolius* and *Excoecaria agallocha*) for comparison and in mangrove sediments for calculation of bio concentration factor (BFC) in Sundarban India. Magnitude of Fe was found highest in the sediments (35371.71 mg kg^{-1}) and plant parts of the three species (a maximum of 11428.0 mg kg^{-1} in the root of *S. caseolaris*). For other heavy metals, plants showed exclusion and selection mainly based on utilization, regardless of their level in the sediments. In most of the cases significant variation of absorption was found between the three species ($F=11.48$ to 157.37; $p<0.001$) and between their plant parts ($F=10.98$ to 338.03; $p<0.001$). *S. caseolaris* was found to be a less potential heavy metal accumulator than the other two species, except for Fe and Zn in the root. Irrespective of the magnitude of the heavy metals, other species showed significant correlations ($r = 0.509$ to 0.961; $p<0.001$) between heavy metal accumulations, exclusively due to chemical reason, whereas *S. caseolaris* showed significant correlations ($r=0.554$ to 0.926; $p<0.001$) between each and every heavy metal, which signifies similar mode of absorption pattern regardless of their utilization. This nonbiased manner of heavy metal accumulation pattern may help the species to withstand in the polluted areas.

Key words

Sundarban ecosystem, Heavy metals, Mangroves, Absorption

Introduction

The problem of disposal of wastewater containing heavy metals is well recognized. (Tam and Wong, 1996). Since heavy metals cannot be degraded biologically, they are often transferred and concentrated into plant tissues from soils and slugs and may pose long-term damaging effects on plants. Nevertheless, different plants react differently to wastewater irrigation; some are more resistant to heavy metals (Yim and Tam, 1999) while others are not. Heavy metal absorption has been found to be responsible often for large scale decline of forest (Gawel *et al.,* 1996). Higher levels of heavy metals in tropical plants and animals can also cause a variety of acute and chronic effects in humans and other vertebrates (Raikwar *et al.*, 2008). Consequently, heavy metals pose a potential threat to various terrestrial and aquatic organisms including human health (Hsu *et al.*, 2006). Human impact on environment can be scaled by the measurements of heavy metals in soil, plants and animals because metal pollution adversely affects the density and diversity of biotic communities including human (Mountouris *et al.,* 2002; Hsu *et al.*, 2006).

Heavy metals are one of the major pollutant classes which accumulate in mangrove ecosystems due to proximity to urban development centers (Harbison, 1986). Mangrove forests, a complex

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inter tidal ecosystem distributed in the tropics and subtropics, appear to possess a remarkable capacity to retain heavy metals (Dwivedi and Padmakumar, 1983; Tam and Wong, 1993). Mangrove forests play an important role in the biogeochemistry of trace metal contaminants in tropical coastal areas, either as sinks or sources for these contaminants (Lacerda *et al.*, 1993; Soto-Jiménez and Páez-Osuna, 2001). Most mangrove tree species have developed strategies to minimize high metal uptake, including metal exclusion through rhizosphere oxidation and preferential metal fixation within root tissues (Doyle and Otte, 1997; Ong Che, 1999).

Around 11,516 small and large factories of the city which produces toxic chemicals dispose their effluent, mostly untreated, find their way into the Kulti river lock gate, located 35 km south east of the city, (Mitra *et al.*, 1999) which happens to be situated in the northern boundary (Dampier-Hodges line) of the tidally influenced mangrove ecosystem of Sundarban.

Sonneratia caseolaris is one of the important mangrove species of the study area. It is not a very common species of Sundarban because of its lesser salt tolerance (~10 ppt) capacity. IUCN has enlisted the species under "Least Concern" category, as per their assessment in 2008, since the overall range of the plant has declined in many areas due to habitat loss or extraction, but not enough to reach any of the threatened category thresholds. This plant has been rarely studied for their heavy metal absorption pattern though it is known to occur at intertidal polluted waters (Guha Bakshi and Naskar, 1991). *Excoecaria agallocha* and *Acanthus ilicifolius* are two other mangrove species commonly found in this area as well as in entire Sundarban. The present paper intends to discuss the accumulation of heavy metal in *S. caseolaris, E. agallocha* and *A. ilicifolius*.

Materials and Methods

Mangrove plant parts were collected from Ghushighata (22° 31' 20.6"N latitude, 88° 41' 14.8" E longitude) situated in the outfall region of the Kolkata metropolitan sewage canal systems, West Bengal, India (Fig 1). In order to investigate the bio-concentration levels of heavy metals, leaves were plucked from ten different plants of the same species. Stem and root samples were scraped out from the same plants without destroying the plants. All the samples were collected between 8:00 to 11:00 am in the month of February, 2011. The collected plant parts were stored in separate zip-lock plastic bags and transported to the laboratory in an ice box for processing on the same day.

The plant parts were washed with double distilled water and kept at dry oven overnight with temperature fixed at 105°C. The samples were digested with concentrated nitric acid and hydrogen peroxide at 90°C (MacFarlane *et al.*, 2003) and volume was made up to 25 ml. The samples were analyzed in an atomic absorption spectrophotometer (model no. AA50–VARIAN) in dry weight basis followed by the digestion method. Three replicate samples were run for each data to achieve the best possible consistent absorbencies. The average of replicates was taken for each heavy metal concentration. The absorbance values of blank samples were estimated to minimize the error and extract values with fine precision. Eight elements Fe, Cu, Zn, Co, Pb, Ni, Cd and Cr were studied. Each and every concentrations were expressed in parts per million (ppm). All reagents and standards used were of analytical grade. Bio concentration factor (BCF) was calculated using the formula given by Agoramoorthy *et al.* (2008).

Statistical analysis was done by MINITAB software (version 13). Pearson correlation was done to find out the correlation between each heavy metal with respect to each other in each mangrove species. ANOVA was performed to determine whether the intra and inter specific accumulation of the different heavy metals were significant or not.

Results and Discussion

The range of heavy metal concentration in the three plant parts of the mangroves and sediments are detailed in Table 1. Table 2 reflects that Fe and Cr were the two most abundant heavy metal in the mangrove sediments. Out of these two, Fe was observed to be the mostly absorbed one in all the plants and its subsequent parts, whereas, Cr happens to be much less preferred by the mangroves. Fe, Zn and Cu occupied the first three places in terms of abundance in the plant parts, with the leaf of *S. caseolaris* being the only exception, where Ni was replaced by Cu. High concentration of Fe could be due to the presence of iron plaques on the roots. Plaques are formed when the roots of mangrove plant leak oxygen and oxidize the rhizosphere sediments. This, in turn, leads to oxidation of the Fe and Mn in the soil and the deposition of Fe on the roots (Mendelssohn *et al.*, 1995). Ni and Pb were the fourth and fifth heavy metal absorded in the mangrove parts except the leaves of *S. caseolaris* and roots of *A. ilicifolius* and *E. agallocha*. Co, Cr and Cd was found to occupy the sixth, seventh and eighth position of preferential absorption order

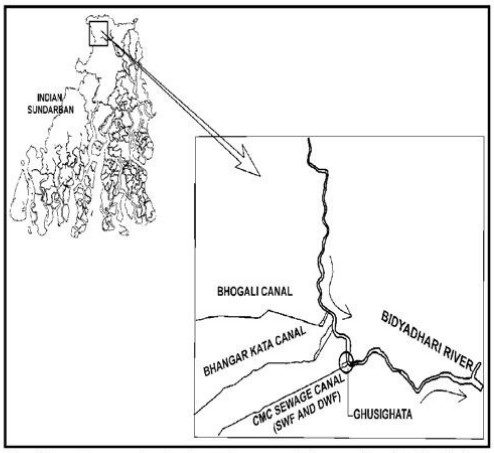

Fig. 1: Location map showing the study area and the sampling site Ghushighata

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Table- 1: Concentration of heavy metals (ppm) in different plant parts of mangrove species and sediment of Sundarban area

Plant	Plant parts	Cr	Pb	Zn	Cd	Ni	Cu	Co	Fe
Sonneratia caseolaris									
	Root	1.926	3.969	19.585	1.214	3.143	4.965	2.427	11428.0
		(1.10-2.80)	(1.99-5.80)	(15.66-21.66)	(0.66-1.52)	(2.32-4.22)	(3.53-6.92)	(1.31-3.55)	(6763.16-15922.06)
	Stem	0.526	0.775	4.151	0.5429	1.018	1.193	0.7198	228.50
		(0.39-0.89)	(0.40-1.64)	(2.88-5.44)	(0.44-0.66)	(0.39-1.70)	(0.73-1.56)	(0.44-0.90)	(130.83-316.48)
	Leaf	1.064	1.8352	12.6890	0.5665	2.6842	2.2260	1.3114	521.40
		(0.94-1.33)	(0.98-2.75)	(10.83-14.87)	(0.44-1.09)	(1.2-3.17)	(1.94-2.71)	(0.90-1.78)	(454.56-665.28)
Acanthus ilicifolius									
	Root	3.511	3.5003	15.9071	2.0058	6.0018	15.6801	3.5057	2813.60
		(2.16-5.82)	(1.95-4.79)	(11.22-18.86)	(.90-2.77)	(2.47-9.19)	(11.86-19.18)	(2.86-5.68)	(1945.90-3872.91)
	Stem	1.309	3.6981	9.6699	1.3324	3.4037	13.6181	2.7398	456.51
		(0.67-2.48)	(2.11- 5.67)	(7.78 – 12.06)	(0.56 – 2.29)	(2.40 – 4.57)	(8.44-19.52)	(1.95-4.18)	(241.30-785.82)
	Leaf	2.3839	4.2795	33.159	0.8915	4.0569	8.321	2.533	669.91
		(1.47-3.62)	(2.97-6.28)	(27.49-45.40)	(0.68-1.35)	(2.61-5.31)	(7.15-10.54)	(1.57-3.95)	(335.78-1242.77)
Excoecaria agallocha									
	Root	7.153	4.499	16.788	4.398	7.004	17.371	4.2894	6248.2
		(5.47-9.60)	(3.14-6.16)	(13.28-21.30)	(3.19-6.79)	(5.74-10.83)	(12.68-23.14)	(2.09-9.09)	(3038.18-9174.27)
	Stem	0.690	1.920	15.095	0.770	2.105	5.716	1.7186	207.21
		(0.39-1.05)	(1.01-3.55)	(11.57-18.29)	(0.36-1.17)	(0.67-3.02)	(3.98-9.96)	(1.00-2.56)	(101.74-360.90)
	Leaf	0.953	5.423	15.987	0.666	3.410	12.218	2.5938	750.00
		(0.46-1.57)	(3.39-7.67)	(11.75-20.31)	(0.48-1.04)	(2.62-4.48)	(9.30-15.29)	(1.85-3.29)	(445.53-981.64)
Mangrove sediment		141.062	29.703	97.456	2.587	42.949	39.534	18.782	35371.71
		(137.51-143.43)	(29.47-30.14)	(93.18-99.69)	(2.54-2.62)	(42.75-43.14)	(38.41-40.38)	(18.32-19.30)	(32648.36-38353.79)

Table- 2: Relative absorption of different heavy metals by three mangrove plants and sediments of Sundarban area

Mangrove plant	Plant parts		
	Root	Stem	Leaf
Sonneratia caseolaris	Fe>Zn>Cu>Pb>Ni>Co>Cr>Cd	Fe>Zn>Cu>Ni>Pb>Co>Cd>Cr	Fe>Zn>Ni>Cu>Pb>Co>Cr>Cd
Acanthus ilicifolius	Fe>Zn>Cu>Ni>Cr>Co>Pb>Cd	Fe>Cu>Zn>Pb>Ni>Co>Cd>Cr	Fe>Zn>Cu>Pb>Ni>Co>Cr>Cd
Excoecaria agallocha	Fe>Cu>Zn>Cr>Ni>Pb>Cd>Co	Fe>Zn>Cu>Ni>Cu>Pb>Cd>Cr	Fe>Zn>Cu>Pb>Ni>Co>Cr>Cd
Mangrove sediment	Fe>Cr>Zn>Ni>Cu>Pb>Co>Cd		

respectively in the leaves of the three mangrove species. In a nutshell, the essential microelements acquired higher priority irrespective of their position in the sediment and the non-essential ones showed the same order of uptake.

The order of magnitude for BCF (Table 3) was as follows : root > leaf > stem. Root BCF of *S. caseolaris* was found to be highest in case of Fe and Zn compared to all the plant parts of other mangroves, whereas, for all other heavy metals *E. agallocha* showed highest root BCF. *S. caseolaris* was reported to be a less salt tolerant plant (~ 10 ppt), whereas other two were found to thrive in almost all salinity regimes of the Sundarbans. In most of the plant parts, BCF for *S. caseolaris* was found to be lesser in magnitude relative to the other two species, as it is commonly recognized that the endurance of mangrove to heavy metals is closely related to their endurance to salt (Zheng, 1997). BCF for Cd exhibited higher (>0.2) values in leaf, stem and root of all the species, as Cd is a comparatively mobile element than other heavy metals, easily absorbed by roots and transported to shoots (Sêkara *et al.*, 2005). It is thought to enter the roots easily, and move slowly to the stem, leaves, and reproductive organs of plants (Lian *et al.*, 1999). Apart from Fe, essential microelements like, Zn, Cu and Co showed higher (≈ 0.1) BCF in all the plant parts of *E. agallocha* and *A. ilicifolius*, but it was found to be higher only in the root in case of *S. caseolaris*. BCF for Cr was found to be insignificant in all the plant parts of the three species. Other heavy metals showed distinct partitioning pattern in all the three species.

Translocation factor (TF) of metals showed indistinctive trend in all the species. TF was highest in all the cases in *A. ilicifolius* except for Cd and Cu. Pb and Zn was found to accumulate in the leaves of *A. ilicifolius* and *E. agallocha* nearly same or beyond the concentration available in the root. Zn is an essential plant micronutrient, mobile and tends to accumulate in mangrove tissue (Shete *et al.*, 2007). As a nutrient, its uptake and allocation to plant organs such as photosynthetic leaf tissue is high and active (Baker and Walker, 1990). On the other hand, high concentration of Pb is justified as it is a multimedia pollutant and its high concentrations in roots may result

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Table- 3: Bio concentration factor (BCF) and Translocation factor (TF) of different plant parts in mangrove plants of Sundarban area

Metals	Mangroves											
	Sonneratia caseolaris				*Acanthus ilicifolius*				*Excoecaria agallocha*			
	Root (BCF)	Stem (BCF)	Leaf (BCF)	TF	Root (BCF)	Stem (BCF)	Leaf (BCF)	TF	Root (BCF)	Stem (BCF)	Leaf (BCF)	TF
Cr	0.0136	0.004	0.007	0.552	0.025	0.009	0.017	0.679	0.051	0.005	0.007	0.133
Pb	0.134	0.026	0.062	0.462	0.118	0.124	0.144	1.223	0.151	0.065	0.183	1.205
Zn	0.201	0.043	0.130	0.648	0.163	0.099	0.340	2.084	0.172	0.155	0.164	0.952
Cd	0.469	0.210	0.219	0.467	0.775	0.515	0.344	0.444	1.610	0.298	0.257	0.151
Ni	0.073	0.023	0.062	0.854	0.140	0.079	0.094	0.676	0.163	0.049	0.079	0.487
Cu	0.126	0.030	0.056	0.448	0.397	0.344	0.210	0.531	0.439	0.145	0.309	0.703
Co	0.129	0.038	0.070	0.540	0.187	0.146	0.135	0.723	0.228	0.091	0.138	0.605
Fe	0.323	0.006	0.015	0.046	0.079	0.013	0.019	0.238	0.177	0.006	0.021	0.120

not just from soil and water but also from atmospheric inputs from industrial processes and combustion of fuels and waste materials which have been absorbed by the foliage (Ong Che, 1999). The higher concentration of Zn and Pb in the leaves of mangrove species can be further justified by the fact that despite some physiological differences in Na^+ uptake among species, patterns of metallic cation (Pb^{2+} and Zn^{2+}) uptake by roots and its consequent translocation to the shoots were broadly similar for both salt secreting (*A. ilicifolius*) and non-secreting species (*E. agallocha*) (MacFarlane *et al.*, 2007). The results of ANOVA showed the absorption and accumulation of heavy metals were significantly different between same plant parts of different species ($F = 11.48$ to 157.37; $p < 0.001$) and between different plant parts of the same species ($F = 10.98$ to 338.03; $p < 0.001$) for a given metal, with few exceptions.

The positive correlations (Table 4, 5 and 6) common for three plants were between Ni with Cr and Cd, between Fe with Cr, Cd, Ni, Cu,Co and between Cd with Cu. The elements that showed significant positive correlation were transition metals which have capability of forming stable co-ordination complexes and hence have higher adsorbing power. Moreover, Fe, Co, Cu and Ni all belong to the same period in the periodic table with similar ionic radius; and generally exhibit +2 or +3 variable valences due to which they have closely equal ionic potential.

The absorption of heavy metals generally occurs either by passive diffusion by virtue of concentration gradient, or by active transfer against any concentration and/ or electrochemical gradient (Stroinski, 1999). In case of *S. caseolaris*, all the heavy metals have strong correlation with each other, which indicates absorption of metals through passive diffusion. In the case of other two mangroves, no significant correlation can be observed in different metals except between those having similar ionic radii, which indicates active transfer to be the mechanism for metal absorption. Active transfer processes

Table- 4: Correlation matrix (Pearson correlation) of different heavy metals absorbed by different plant parts of *Sonneratia caseolaris*

	Cr	Pb	Zn	Cd	Ni	Cu	Co
Pb	**0.864** **0.000**						
Zn	**0.870** **0.000**	**0.833** **0.000**					
Cd	**0.779** **0.000**	**0.732** **0.000**	**0.757** **0.000**				
Ni	**0.757*** **0.000**	**0.756** **0.000**	**0.861** **0.000**	**0.585*** **0.001**			
Cu	**0.926** **0.000**	**0.872** **0.000**	**0.913** **0.000**	**0.896*** **0.000**	**0.785** **0.000**		
Co	**0.832** **0.000**	**0.738** **0.000**	**0.902** **0.000**	**0.845** **0.000**	**0.773** **0.000**	**0.914** **0.000**	
Fe	**0.703*** **0.000**	**0.733** **0.000**	**0.800** **0.000**	**0.822*** **0.000**	**0.554*** **0.000**	**0.843*** **0.000**	**0.856*** **0.000**

n=30, r value and their corresponding p value; Bold font indicates significant correlation; *indicates correlations between heavy metals common in all the three plants

Table- 5: Correlation matrix of different heavy metals absorbed by different plant parts of *Acanthus ilicifolius*

	Cr	Pb	Zn	Cd	Ni	Cu	Co
Pb	0.046 0.810						
Zn	0.186 0.325	0.335 0.071					
Cd	0.464 0.010	-0.029 0.880	-0.376 0.040				
Ni	**0.582*** **0.001**	-0.211 0.263	0.016 0.934	**0.509*** **0.004**			
Cu	0.184 0.331	-0.125 0.510	**-0.600** **0.000**	**0.676*** **0.000**	0.219 0.245		
Co	0.419 0.021	-0.046 0.809	-0.160 0.398	0.334 0.071	0.280 0.134	0.311 0.095	
Fe	**0.720*** **0.000**	-0.113 0.742	-0.133 0.484	**0.587*** **0.001**	**0.598*** **0.003**	**0.544*** **0.002**	**0.610*** **0.000**

n=30, r value and their corresponding p value. Bold font indicates significant correlation; * indicates correlations between heavy metals common in all the three plants

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Table 6 : Correlation matrix of different heavy metals absorbed by different plant parts of *Excoecaria agallocha*

	Cr	Pb	Zn	Cd	Ni	Cu	Co
Pb	0.313						
	0.092						
Zn	0.169	0.243					
	0.371	0.195					
Cd	**0.856**	0.199	0.214				
	0.000	0.291	0.257				
Ni	**0.849***	0.387	0.289	**0.768***			
	0.000	0.034	0.121	**0.000**			
Cu	**0.784**	**0.604**	0.341	**0.711***	**0.780**		
	0.000	**0.000**	0.065	**0.000**	**0.000**		
Co	**0.643**	0.337	0.197	**0.724**	**0.718**	**0.763**	
	0.000	0.069	0.296	**0.000**	**0.000**	**0.000**	
Fe	**0.961***	0.316	0.175	**0.901***	**0.851***	**0.808***	**0.715***
	0.000	0.089	0.354	**0.000**	**0.000**	**0.000**	**0.000**

n=30, r value and their corresponding p value. Bold font indicates significant correlation ; * indicates correlations between heavy metals common in all the three plants

generally occurs through a cation channel in the cell membrane of roots, specially meant for the uptake of some essential metals. Some cations having similar ionic potentials passes through those channels owing to similar ionic radii (Singh, 2005) which justify the correlations observed in case of *A. ilicifolius* and *E. agallocha*.

It can be concluded, that irrespective of the concentration of a particular heavy metal in the sediment, the mangroves under study preferentially absorb the metals in different plant parts in accordance with the physiological necessity of the plant and/ or mobility of the metal. Among the three species studied, *S. caseolaris* being less salt tolerant, absorbed heavy metal in lesser amount. Although, non-discriminating mode of absorption of all heavy metals may help the plant to withstand in the inner estuarine polluted environment.

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