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RESEARCH PAPER

Heavy Metal Accumulation in the Mangrove Ecosystem of South Gujarat Coast, India

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Abstract

The mangrove ecosystem in South Gujarat estuaries constantly reel under the pressure of pollution owing to the rapid industrialization. Hence, this study was carried out to assess the impacts of heavy metals coming into the system through the waste discharges on the overall mangrove health in selected estuaries of the region. The concentrations of different heavy metals such as Pb, Ni, Cr, Cd, Zn, Cu, Fe and Hg were measured in the sediments and tissues of *Avicennia marina* (Forssk.) Vierh. (Family: Acanthaceae) in seven estuaries of South Gujarat. The results revealed that despite the relatively high heavy metal accumulation (Cr > Cu > Zn > Ni > Pb > Cd > Hg) in the mangrove sediments of the study sites, *A. marina* plants selectively uptake only Cu and Zn and tend to avoid rest of the heavy metals. The analysis of the mangrove sediments indicated a positive correlation between the organic matter and clay content with the heavy metals. No visible impact of heavy metal on the morphology of the plants could be observed and the present paper discusses how the plants have adopted to the environment.

Keywords: Industrial pollution, bioaccumulation, **e**stuaries, impacts.

Introduction

The estuarine and coastal areas are the zone of interaction between fresh and marine waters hence, are highly complex owing to the tidal currents and waves (Morris *et al*., 1995). The estuaries are rightly considered to be the most important ecosystems as they are a vital site for primary production (Bricker *et al*. 2008) and a suitable habitat for numerous species (Lotze, 2010). The most characteristic vegetation present in the estuarine region is mangrove. The mangroves are woody plant communities situated in the intertidal zone of tropical, sub tropical coasts, and play a very important role as biological resources in the coastal ecosystems (Linn, 1988; Zheng, 1995; Peng *et al*., 1997). Besides, they also provide various important ecosystem services such as shoreline protection, sheltering and provide nutrients to large diversity of organisms, supporting livelihoods, etc.

However, this unique ecosystem is constantly under the brunt of anthropogenic activities such as agricultural run-off, urban sewage industrial effluents, mining, port activities, etc. Among the various types of pollutants released from such activities, heavy metals are one of the most serious pollutants owing to their toxicity, persistence and bioaccumulation problems (Macfarlane & Burchett, 2002; Lindsey *et al*., 2006; Vane *et al*., 2009; Lal Shah, 2010). The metal contamination is a major environmental problem as the metals in contaminated sediments may accumulate in the various organisms of the estuarine ecosystem and ultimately enter the food chain, thereby affecting the human well-being (Shakeri & Moore, 2010). The concentrations of heavy metals in the sediments usually exceed that of the overlying water (Zabetoglouet *et al*., 2002) and the high concentrations of these metals in water and sediments affect both plants and animals (Doganlar & Atmaca, 2011). The accumulation of heavy metals in the mangrove ecosystems has been reported and studied in a number of countries including China (Peng *et al*., 1997); Singapore (Cuong *et al*., 2005); Iran (Shirvani Mahdavi *et al*., 2012) and Oman (Keshavarz *et al*., 2012).

In India, the mangroves are found growing luxuriantly along the east and west coasts with their highest diversity and luxuriance being in the Sunderbans in West Bengal state. Among the west coast states, Gujarat is bestowed with the longest coastline of about 1600 kms which also serves as the meeting point for numerous west flowing rivers. The state has witnessed humongous industrial development in the last few decades. In the different areas around coast of South Gujarat, the industrialization had taken up in early seventies. There are several industrial areas like Vapi GIDC, in the region much of these are located in the vicinity of rivers and estuaries for the obvious convenience of discharging the industrial waste. The region has become the focal centers of many large scale industrial units chiefly belonging to dyes, manufacturing and engineering, textiles, papers, chemicals and petrochemicals, pharmaceuticals, ship building, diamond processing, etc. Among these, the discharge from chemical, paper, pharmaceutical and food product based industries is considered as chief source metals such as Pb, Cr, Cu, Zn, Ni, Hg and Cd into the water sources (Radic *et al*., 2010; Al-Shami *et al*., 2010; Devi *et al*., 2010).

Though there are several laws established for treating the wastes before discharging in natural environment, these are often dumped indiscriminately into nearby freshwater sources which ultimately end up in the estuaries. Hence, the rising pollution levels and deterioration of natural habitats prompted this study to be carried out to assess the impacts of heavy metals, entering the estuaries and overall health of the mangrove ecosystem in selected estuaries of south Gujarat coastal region.

Materials and Methods

Study area

Seven different estuarine sites (Figure 1) were selected for the study on the south Gujarat coast representing seven different rivers, viz., Varoli (site-1), Damanganga (site-2), Kolak (site-3), Par (site-4), Auranga (site-5), Purna (site-6) and Ambica (site-7). All of these are west flowing perennial rivers draining into the Arabian Sea on South Gujarat coast between Umbargam (S) to Surat (N). This region is characterized by semi-arid to dry sub-humid climatic conditions with the average rainfall ranging from 800–1000 mm. Most of these estuaries are surrounded by small villages/towns wherein some people are involved in fishing and sand extraction activities. There are ten mangroves species reported from these estuaries viz. *Avicennia marina* var. *marina*, *Avicennia officinalis* L., *Sonneratia apetala*, *Acanthus ilicifolius*, *Rhizophora mucronata*, *Ceriops tagal*, *Bruguiera cylindrica*, *Lumnitzera racemosa*, *Excoecaria agallocha* L. and *Aegiceras corniculatum*. Apart from this there are six species of salt marsh plants from the area (Bhatt 2009).

Sampling and Analysis

Among the mangrove species *Avicennia marina* (Forssk.) Vierh. dominates more than 80% of the study region. Hence, this species was selected for the heavy metal analysis in the present study. The fresh plant material at each of the estuary collected in the months of May and November in the year 2015. The leaves, twigs and pneumatophores of *A. marina* were collected from at least 5-8 different individuals with similar girth at breast height at each site. All these plant materials were then packed in air tight clean

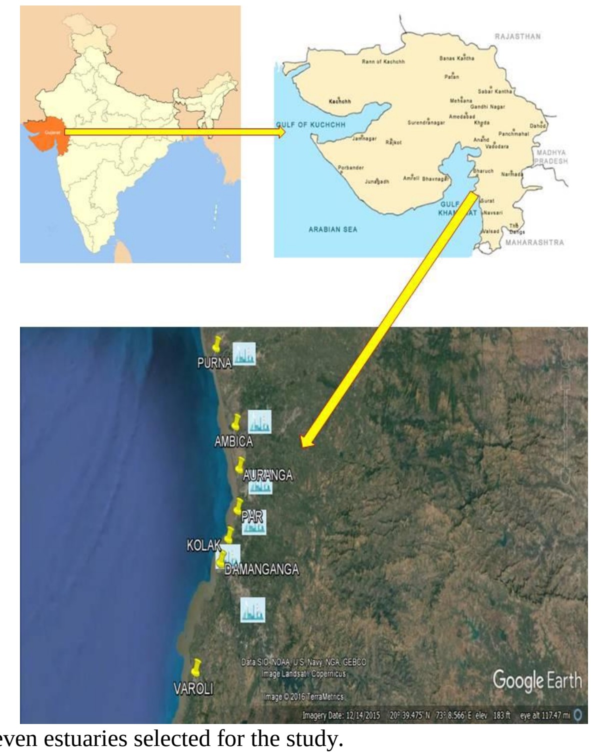

Figure 1. Map showing the seven estuaries selected for the study.

plastic bags and brought to the laboratory for further analysis. These plant parts were thoroughly washed with distilled water and subsequently put in the oven at 48°C for 3-4 days till completely dried. These oven dried samples were homogenously powdered and further packed in labeled air tight plastic bags. The sediment samples were collected using grab sampler from 3-4 different places at each study site brought to laboratory and air-dried. Further they were oven dried at 48°C for 2 days to ensure all remaining moisture is evaporated (Defew *et al*., 2005). The texture analysis for the sediment samples was carried out using method prescribed by Folk (1965) whereas the organic matter for soil sediments was estimated using Rowell (1994) method.

10 gm of sediment sample from each site was homogenized and stored in air tight labeled plastic bags. Both the dried powdered samples of plant tissues and sediments were thoroughly packed and sent to the Centre for Coastal and Marine Research in Tuticorin for the heavy metals analysis using Inductively Coupled Plasma–Mass Spectrometer (ICP-MS), following (AOAC, 1997) protocol. The mean values with standard deviation for resultant data for the heavy metals were calculated and statistical analysis was performed using the Past3 and SPSS 20.0 statistical software.

The bioconcentration factor (BCF) defined as $BCF=C_{biota} / C_{soil}$, where C_{biota} and C_{soil} are the total metal concentration in biota and soil respectively was calculated. BCF is usually an indicator of phytoremediation capability of the concerned plant species (Chakraborty *et al*., 2013). The Bio-concentration factor was calculated for every metal in the system.

Results

Heavy Metal Accumulation in *Avicennia marina* Tissues

The amount of eight different heavy metals in the plant tissues of *Avicennia marina* from the study sites is depicted in Table 1. The range of heavy metals in the plant parts across the study sites were: Pb: 0.001–0.045 µg/g; Cd: 0.001–0.03 µg/g; Ni: 0.003–0.07 µg/g; Cr: 0–0.05 µg/g; 0.33–14 µg/g; Zn: 0.14–0.7 µg/g; Mn: 0.16–0.82 µg/g and Fe: 1.6–9.5 µg/g. The mean total content of these metals in the plant tissues in the study region was found in the order of Cu (18.481±2.742 µg/g) > Fe (16.058±2.307 µg/g) > Mn (1.377±0.130 µg/g) > Zn (1.172±0.134 µg/g) > Ni (0.092±0.023 µg/g) > Pb (0.053±0.016 µg/g) > Cd (0.047±0.008 µg/g) > Cr (0.021±0.017 µg/g). It can be deduced that the most common trend of metal flow in the plant tissues is in the order of pneumatophores > twigs > leaves with few exceptions. Overall, *A. marina* in the study region was found to accumulate high content of essential heavy metals–Cu, Zn and Fe, as compared to the non-essential heavy metals–Pb, Cd, Cr, Mn and Ni. Figure 2 a & b represent the variation of mean individual content of essential and non-essential heavy metals in the plant tissues across the study sites.

Pb content was found to be relatively high in the plant tissues of sites–2 and 3, whereas the Ni content was found high at sites–1, 3 and 2 followed by other sites. Among all the sites, site 4 showed low mean content of Pb, Cr, Cd and Ni in the mangrove plant. The mean Cu content in mangroves was found to be high at site 3 followed by 4, 2 and 1 sites, while minor variation was recorded at sites–5 to 7. However, the mean Fe content in mangroves showed variation with the high values at sites 7 and 4.

Heavy Metal Accumulation in Mangrove Sediments

The values of Cr, Cu, Zn, Ni, Pb, Cd, Hg in the sediments was recorded as 15–51 µg/g, 20–46 µg/g, 18–42 µg/g, 18–26 µg/g, 8–13 µg/g, 8–13 µg/g and 0–15 µg/g respectively. The order of these metals in the mangrove sediments based on the concentrations level in the sediment was Cr > Cu > Zn > Ni > Pb > Cd > Hg. On comparing the results obtained from the present study with similar studies elsewhere in the world showed, (Table 2), high Cd levels in the mangrove sediments of South Gujarat, while Zn levels was low compared to other similar studies. The levels of Pb Ni, Cr, and Cu levels in the sediments were at par with most other similar studies around different parts of the world (Mackey *et al*., 1992; Goh & Chou, 1997; Wood *et al*., 1997; Ong Che, 1999; Tam & Wong, 2000; Nayar *et al*., 2004; Cuong *et al*., 2005, 2006; Khattak *et al*., 2012). The correlation based cluster analysis for the study sites incorporating heavy metal content is depicted in Figure 4a. All the sites were divided into two clusters–cluster A comprising of Site 1 which was least similar to all the other sites falling into cluster B. Cluster B was further sub-divided into sub-clusters B1 comprising of Site 2 and B2 contained remaining study sites. The heavy metal content in the sediments of sites–3, 5, 6 and 7 was more similar to each other and less similar with that of site 4.

Bio-Concentration Factor for Heavy Metal Accumulation

The BCF values for the different study sites are depicted in Table-3.The pneumatophore BCF ranged from 0.210–0.418 for Cu indicating that the *Avicennia* plants site 4 had the highest potential for Cu uptake from the sediments followed by site 6 (0.301). Similarly the pneumatophore BCF for Zn ranged from 0.012–0.028 with the highest Zn uptake potential again at site 4. The BCF for the remaining four heavy metals was very low and ranged from 0.003–0.005 for Pb, 0.001–0.004 for Ni, 0.002–0.004 for Cd and 0–0.001 for Cr. The correlation based cluster analysis

Table 1. Heavy metal content in the pneumatophores, twigs and leaves of A. marina in the study region, M±S.D., n=2

Site No.	Estuary name	Pb	Cd	Ni	Cr	Cu	Zn	Mn	Fe
CONTENT IN PNEUMATOPHORES (µg/g)									
1	Varoli	0.033±0.004 Sig. 0.049	0.020±0.006 Sig. 0.126	0.071±0.017 Sig. 0.107	0.027±0.038 Sig. 0.500	8.675±0.629 Sig. 0.033	0.610±0.156 Sig. 0.114	0.769±0.067 Sig. 0.039	7.37±0.863
2	Damanganga	0.068±0.003 Sig. 0.019	0.022±0.011 Sig. 0.214	0.048±0.010 Sig. 0.092	0.012±0.016 Sig. 0.472	6.430±1.485 Sig. 0.103	0.490±0.028 Sig. 0.026	0.452±0.101 Sig. 0.100	5.04±1.195
3	Kolak	0.047±0.005 Sig. 0.048	0.030±0.009 Sig. 0.138	0.040±0.004 Sig. 0.048	0.007±0.008 Sig. 0.447	14.105±6.399 Sig. 0.198	0.380±0.014 Sig. 0.017	0.693±0.029 Sig. 0.019	9.09±0.318
4	Par	0.016±0.023 Sig. 0.500	0.023±0.016 Sig. 0.500	0.015±0.021 Sig. 0.500	< DL	4.225±5.975 Sig. 0.500	0.545±0.021 Sig. 0.500	0.635±0.064 Sig. 0.500	8.98±0.502
5	Auranga	0.036±0.022 Sig. 0.262	0.021±0.004 Sig. 0.077	0.031±0.014 Sig. 0.199	0.005±0.007 Sig. 0.500	9.790±0.028 Sig. 0.001	0.630±0.028	0.594±0.239 Sig. 0.176	7.38±0.191
6	Purna	0.035±0.008 Sig. 0.101	0.025±0.016 Sig. 0.264	0.046±0.019 Sig. 0.184	0.019±0.025 Sig. 0.482	10.500±2.701 Sig. 0.115	0.505±0.021 Sig. 0.019	0.577±0.086 Sig. 0.067	7.13±1.018
7	Ambica	0.020±0.028 Sig. 0.500	0.010±0.015 Sig. 0.500	0.017±0.024 Sig. 0.500	0.014±0.020 Sig. 0.500	4.210±5.954 Sig. 0.500	0.420±0.085 Sig. 0.500	0.706±0.036 Sig. 0.500	7.95±0.523
CONTENT IN TWIGS (µg/g)									
1	Varoli	0.008±0.001 Sig. 0.079	0.023±0.002 Sig. 0.042	0.046±0.006 Sig. 0.063	0.001±0.00	5.970±0.905 Sig. 0.068	0.195±0.021 Sig. 0.049	0.244±0.048 Sig. 0.088	3.46±0.346 Sig. 0.053
2	Damanganga	0.013±0.003 Sig. 0.097	0.021±0.002 Sig. 0.046	0.031±0.002 Sig. 0.031	0.002±0.001 Sig. 0.205	8.990±3.111 Sig. 0.153	0.295±0.035 Sig. 0.054	0.544±0.066 Sig. 0.055	4.79±0.594 Sig. 0.106
3	Kolak	0.017±0.004 Sig. 0.096	0.031±0.006 Sig. 0.082	0.057±0.008 Sig. 0.067	0.001±0.00	8.485±1.322 Sig. 0.070	0.455±0.064 Sig. 0.063	0.626±0.135 Sig. 0.0.096	4.37±0.771 Sig. 0.016
4	Par	0.017±0.006 Sig. 0.170	0.015±0.006 Sig. 0.166	0.032±0.001 Sig. 0.020	0.003±0.001 Sig. 0.126	6.130±0.594 Sig. 0.044	0.330±0.057 Sig. 0.077	0.447±0.193 Sig. 0.189	5.79±0.693 Sig. 0.500
5	Auranga	0.019±0.011 Sig. 0.245	0.020±0.006 Sig. 0.144	0.049±0.008 Sig. 0.072	0.002±0.001 Sig. 0.205	8.890±0.834 Sig. 0.042	0.415±0.049 Sig. 0.054	0.618±0.107 Sig. 0.077	7.14±0.318 Sig. 0.012
6	Purna	0.018±0.005 Sig. 0.126	0.024±0.005 Sig. 0.094	0.029±0.004 Sig. 0.056	0.002±0.003 Sig. 0.500	7.955±0.332 Sig. 0.019	0.675±0.078 Sig. 0.052	0.486±0.077 Sig. 0.071	4.91±0.573 Sig. 0.064
7	Ambica	0.016±0.004 Sig. 0.118	0.024±0.006 Sig. 0.120	0.026±0.003 Sig. 0.049	0.005±0.003 Sig. 0.242	9.955±6.470 Sig. 0.274	0.525±0.120 Sig. 0.102	0.419±0.054 Sig. 0.058	7.44±1.252 Sig. 0.500
CONTENT IN LEAVES (µg/g)									
1	Varoli	0.01 ± 0.001 Sig. 0.500	0.002±0.001 Sig. 0.205	0.016±0.002 Sig. 0.061	< DL	0.485±0.035 Sig. 0.033	0.275±0.049 Sig. 0.081	0.269±0.067 Sig. 0.111	3.36±0.240 Sig. 0.032
2	Damanganga	0.001±0.001 Sig. 0.500	0.002±0.000 Sig. 0.217	0.013±0.004 Sig. 0.144	< DL	0.330±0.057 Sig. 0.077	0.165±0.021 Sig. 0.058	0.235±0.038 Sig. 0.073	2.56±0.205 Sig. 0.036
3	Kolak	0.002±0.001 Sig. 0.205	0.003±0.000 Sig. 0.066	0.011±0.002 Sig. 0.090	< DL	0.805±0.177 Sig. 0.098	0.385±0.134 Sig. 0.154	0.216±0.030 Sig. 0.063	2.75±0.156 Sig. 0.025
4	Par	0.002±0.001 Sig. 0.205	0.002±0.000 Sig. 0.192	0.006±0.001 Sig. 0.105	< DL	2.255±0.134 Sig. 0.027	0.205±0.021 Sig. 0.046	0.163±0.033 Sig. 0.089	2.62±0.120 Sig. 0.021
5	Auranga	0.001±0.000	0.002±0.001 Sig. 0.126	0.004±0.001 Sig. 0.090	< DL	1.440±0.099 Sig. 0.031	0.150±0.014 Sig. 0.042	0.168±0.009 Sig. 0.025	1.66±0.219 Sig. 0.059
6	Purna	0.001±0.001 Sig. 0.500	0.004±0.001 Sig. 0.070	0.007±0.001 Sig. 0.090	< DL	1.585±0.205 Sig. 0.058	0.145±0.035 Sig. 0.109	0.245±0.040 Sig. 0.074	2.33±0.279 Sig. 0.057
7	Ambica	0.001±0.001 Sig. 0.500	0.002±0.000 Sig. 0.192	0.005±0.001 Sig. 0.070	< DL	0.885±0.078 Sig. 0.040	0.215±0.021 Sig. 0.044	0.240±0.028 Sig. 0.053	2.52±0.332 Sig. 0.059

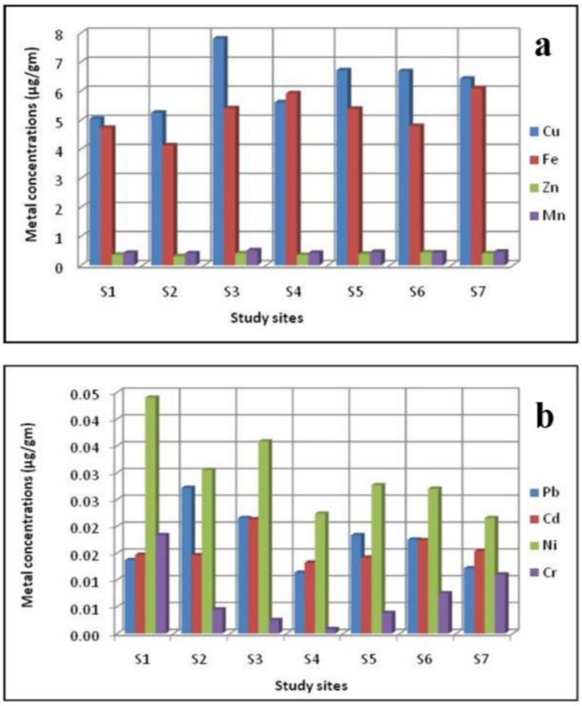

Figure 2. (a & b) Overall mean content of non-essential heavy metals in *A. marina* tissues; (b) Overall mean content of essential heavy metals in *A. marina* tissues.

was performed for the study sites using the BCF values depicted in Figure 4b. Here also, the sites were broadly divided into two main clusters–cluster A comprising of site 1 which was less similar to the other sites in cluster B. In cluster B, Site 2 was again segregated into sub-cluster B1 while the remaining sites were clustered into B2. In this sub-cluster, sites 4 and 7 were similar, sites 5 and 6 in one sub cluster, while site 3 showed distinct character. Furthermore, the metals were clustered into a dendrogram based on their BCF values for the different study sites (Figure 5) into three different sub-clusters which were least similar to each other.

Discussion

Heavy Metal Accumulation In Mangrove Sediments

The non-essential polluting heavy metals Cadmium (Cd) and Lead (Pb) are known to be toxic metals (Kumar *et al*., 2008; Lim *et al*. 2008; Weng *et al*. 2008) with very little (Lane *et al*. 2005; Xu *et al*. 2008) or no nutrient values. Pollution of soils, sediments and waters with Pb and Cd enters the food chain and due to cumulative nature result in wide variety of adverse effects in animals and humans (Sanborn *et al*. 2002; Jacobson and Turner, 1980; Stohs and Bagchi, 1995; Waalkes, 2000). The content of Pb in the sediments of south Gujarat estuaries was found to be in the order of Ambica > Par > Kolak > Purna > Auranga > Damanganga > Varoli whereas the content of Cd in the sediments was in the order of Ambica > Kolak > Damanganga > Auranga > Purna > Varoli > Par. Among these, visible color and odor changes in the water of Damanganga estuary and Kolak estuary could be observed due to the pollution.

The higher concentration of Cd in the sediments as compared to other estuaries of the world can be attributed mainly to the unprecedented industrial development in the surrounding towns and cities. Cd, along with its compounds, is widely used as heat stabilizers for plastics, for corrosion resistance of steel and cast iron, metal plating, phosphate fertilizers, alloy industries and in battery industries (Mahvi & Bazrafshan, 2007). Similarly Pb is an important metal involved in industries such as pulp and paper, petrochemicals, refineries, printing, photographic materials, glass, oil, metal, electronic, alloy and steel industries and storage batteries (Gupta *et al*., 2001; Jalali *et al*., 2002; Conrad & Hansen, 2007). The main industrial belts surrounding the study sites are Vapi, Valsad, Navsari, Bharuch and Surat which are dominated by industrial equipment and electronics manufacturing industries, glass industries, chemicals and pharmaceutical industries along with few industries of plywood, paper, food products and textile. The discharge by these industries into the rivers streams and directly into the estuaries is the chief cause for the higher concentration of heavy metals especially the toxic metals in the study areas.

The texture analysis of mangrove sediments in the study region highlighted that the sediments of site 1 and site 6 were having 100 % clay (Sand and Clay was BDL) followed by site 2 with 98% clay. A higher percentage of silt was found in the sediments at site 7

Table 2. Comparison between the heavy metal content (µg/g) in the mangrove sediments of current study and other similar studies from different parts of the world. The general critical soil concentrations follow Alloway (1990)

STUDY AREA	Pb	Cd	Ni	Cr	Cu	Zn	Reference
South Gujarat	11.22±1.56	10.40±1.75	21.53±2.51	35.46 ±10.5	33.88±7.9	31.91±7.8	Current study
S. BULOH	12.28±5.18	0.181±0.349	7.44±3.46	16.61±7.23	7.06±6.03	51.24±39.97	Cuong *et al*., 2005
S. Khatib Bongsu	30.98±6.16	0.266±0.171	11.65±4.49	32.07±7.67	32.00±14.32	120.23±13.90	Cuong *et al*., 2006
Ponggol estuary	17.3	0.24	6.07	0	34.65	0	Nayar *et al*., 2004
Straits of Johore	42.3±11	0.18±0.06	30.2±6.6	45.2±11.2	30.7±22.5	132.5±52.6	Wood *et al*., 1997
Twenty coastal locations around Singapore	2–60	ND–1.4	0	0	2–204	5–280	Goh and Chou, 1997
Guanabara bay, Brazil	165.5–169.5	0	0	37.4–43.4	79.6–91.7	447.5–505.1	Kehrig *et al*., 2003
Mai Po, Hong Kong	161.6–219.8	0.5–0.6	65.3–66.0	7.8–17.4	41.9–49.8	277.2–321.2	Ong Che, 1999
Deep Bay, Hong Kong	80	3	30	40	80	240	Tam and Wong, 2000
Mazatlan harbor, Mexico	<150	< 2	6.1–30.3	7.6–42.5	7.7–90.9	46.4–347.8	Soto-Jimenez and Paez-Osuna, 2001
Brisbane river, Australia	20.1– 81.9	<0.1–1.9	0	13.3–54.3	3.1–30.2	40.8–144.0	Mackey *et al*., 1992
Karachi coastal area	0.01 - 0.045	0 - 0.1	0	0.001 - 0.085	0.007 - 0.04	0 - 0.1	Khattak *et al*. 2012
General critical soil concentration	400	8		100	125	400	Alloway, 1990

with 87.03% followed by site 4 (53.46%). The average organic matter content was 112.14 mg/g having slight variation at different study sites, highest being in site 6 (122.27 mg/g) and lowest was in site 3 (108.08 mg/g). Similarly the average organic carbon in the study region was 65.04 mg/g, highest being 70.92 mg/g at site 6 and lowest being 61.81 at site 3. Pearson's correlation matrix was obtained for the organic carbon content, sediment texture components and heavy metals (Table 4). It was clearly evident that the clay content in the sediments was positively correlated with the organic carbon content (0.455). With respect to the heavy metals, a significant positive correlation was observed between Pb and clay content (0.870) followed by Zn and clay (0.749), Cr and Silt (0.608), Cd and sand (0.520), Ni and clay (0.434). The same metals also showed a positive correlation with organic carbon. The organic carbon content of sediments were also positively correlated with Ni and Hg (0.401). This result was verified and explained by Raj *et al*. (2013), wherein the metals Cd and Pb showed positive correlation with silt and clay fraction of the sediments in Mahanadi estuary suggesting that the fine sediments, i.e., silt and clay type sediments which are rich in organic content have higher cation exchange capacity and are able to trap

Table 3. Bio-Concentration factor (BCF) for the different heavy metals across the study sites

	Pb	Cd	Ni	Cr	Cu	Zn	Hg
S1	0.003	0.002	0.004	0.003	0.216	0.019	0.001
S2	0.005	0.003	0.003	0.001	0.244	0.012	0.000
S3	0.004	0.004	0.002	0.000	0.210	0.013	0.000
S4	0.003	0.002	0.001	0.000	0.418	0.028	0.000
S5	0.004	0.002	0.002	0.000	0.293	0.018	0.000
S6	0.003	0.003	0.002	0.001	0.301	0.017	0.001
S7	0.004	0.003	0.002	0.001	0.249	0.019	0.000

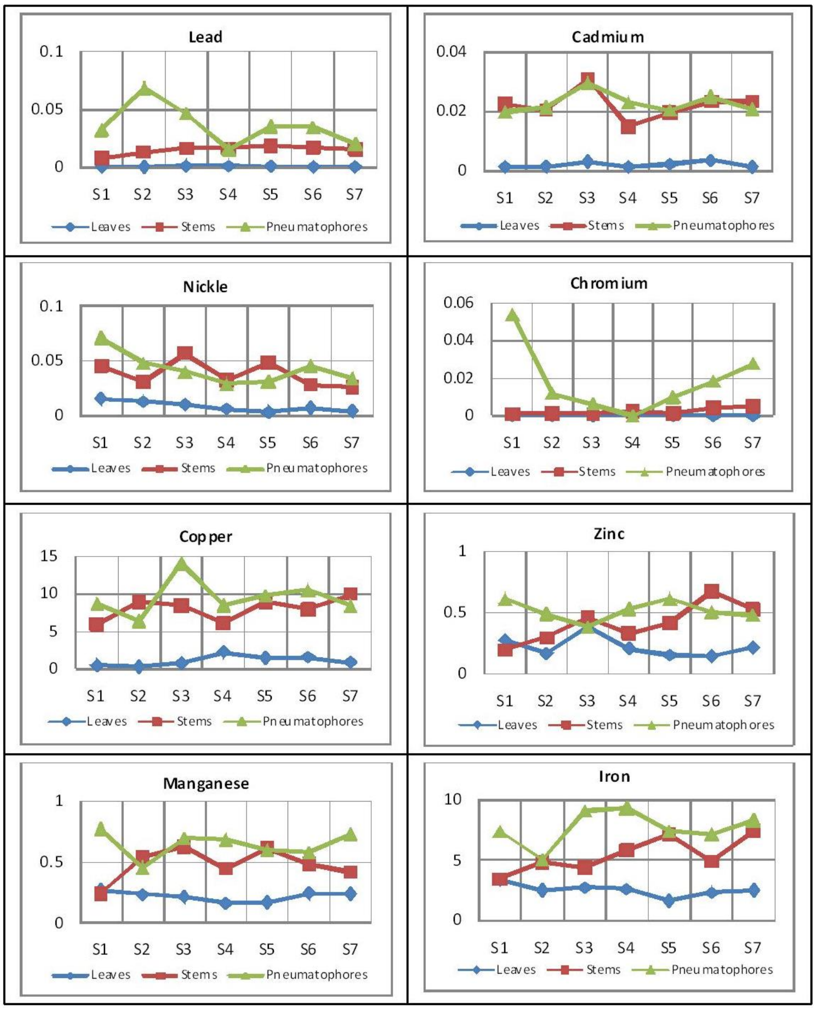

Figure 3. Mean content (μg/g) of eight different heavy metals in *A. marina* tissues of the study sites.

metal rich sediments. In contrast to this, the sand rich mangrove sediments have little ability to retain metal ions.

Heavy Metal Accumulation in Mangrove Plant Tissues

Upon comparing the cluster analyses of heavy metals in the mangrove sediments and the BCF values for the study sites, it was evident that sites 1 and 2 were different from each other than the remaining sites. The remaining sites in these two clusters were also grouped in a more or less similar fashion clearly indicating that the amount of heavy metals in the mangrove sediments has a direct impact on the bioaccumulation potential of the mangroves in that site. Fluctuating climatic conditions (rainfall and temperature), soil edaphic factors, available nutrients in the substrate and concentration of other nutrients can affect the nutrients concentration considerably in plant components and sediments as well as mineral metabolism and uptake of nutrients by the roots (Kabata-Pendias & Pendias, 1984; Jones, 1998; Sahel, 2013). Furthermore, the cluster analysis dendrogram of heavy metals clearly indicate that the accumulation of non-essential metals was totally different from the essential metals. The formation of three sub-clusters reflected a relationship between the accumulation potential of Pb & Cd, Cu & Zn and Ni, Cr & Hg.

Many studies around the world have reported elevated concentrations of non-essential toxic heavy metals in unpolluted and polluted mangrove ecosystems, which suggest that there is a possible function of sequestering selective toxic metals, especially with respect to Pb (Ong Che, 1999). Moreover, it is reported that the heavy metal concentrations in the mangrove species tissues are usually associated with the concentration of these

Table 4. Pearson's Correlation between sediment texture, organic carbon and heavy metals

Parameter	SAND (%)	SILT (%)	CLAY (%)	OC (mg/g)	Cu (µg/g)	Zn (µg/g)	Cr (µg/g)	Ni (µg/g)	Pb (µg/g)	Cd (µg/g)	Hg (µg/g)
SAND	1										
SILT	.582	1									
CLAY	-.620	-.999**	1								
OC	-.242	-.456	.455	1							
Cu	-.605	-.106	.137	-.276	1						
Zn	-.740	-.732	.749	.124	.460	1					
Cr	.298	.608	-.604	-.110	.026	-.418	1				
Ni	-.486	-.420	.434	.401	.334	.052	.126	1			
Pb	-.475	-.873*	.870*	.182	.327	.780*	-.731	.147	1		
Cd	.520	-.241	.203	.095	-.600	-.315	-.534	-.117	.261	1	
Hg	-.583	-.340	.362	.401	.033	.614	-.457	-.260	.317	-.294	1

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

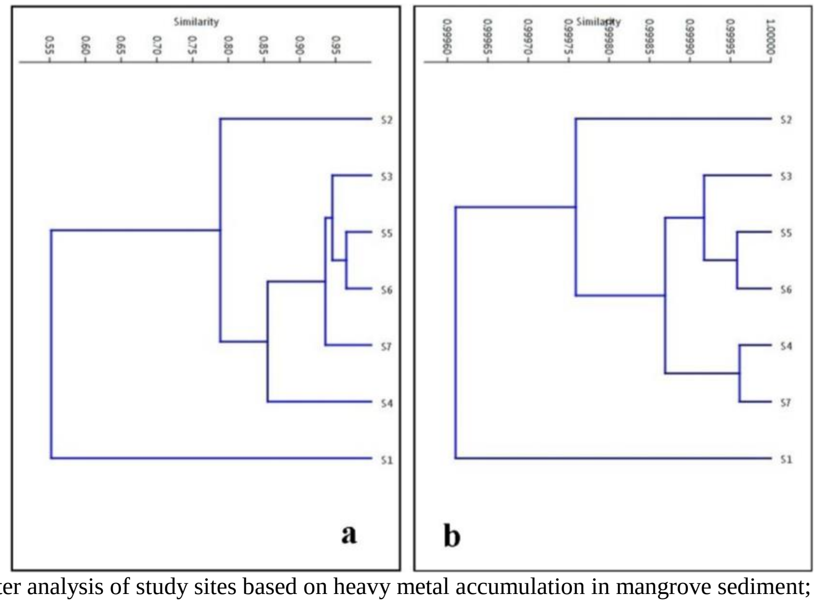

Figure 4. (a) Cluster analysis of study sites based on heavy metal accumulation in mangrove sediment; (b) Cluster analysis of study sites based on bioaccumulation potential of *A. marina.*

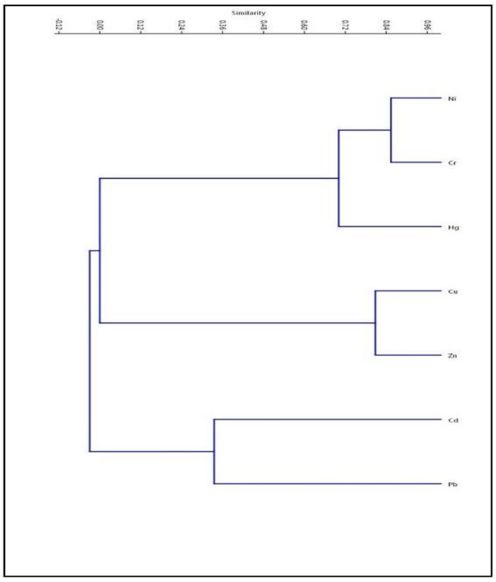

Figure 5. Cluster analysis of heavy metals based on their BCF in different study sites.

metals in the mangrove sediments (Machado *et al*. 2002). The heavy metals like Pb and Cd were found to be in micro concentrations in the *A. marina* tissues of South Gujarat estuaries despite five hundred times higher concentration in the sediments. This result clearly indicates that the mangrove tissues in this study region have developed a selective mechanism of avoiding the uptake of non-essential heavy metals from the ecosystem. Such major variations can be most likely due to the physiological differences and variations in accumulation strategies of different plant species (Defew *et al*., 2005). It is also speculated that *Avicennia marina* could be more tolerant to heavy metal by developing several adaption mechanisms including avoiding the uptake of metals actively and exclusion of ions (Burchett *et al*., 2003).

Furthermore, the concentrations of different heavy metals in the plant tissues is largely influenced by the metabolic requirements for essential micro-nutrients such as Cu and Zn, whereas the non-essential metals such as Cd tend to be excluded or compartmentalized (Baker & Walker, 1990). In this study too, the uptake of Zn and Cu is higher when compared to other non-essential heavy metals and this was also validated by the bio-concentration factors, which were of some significant value for Zn and Cu while negligible for remaining metals. Cu is an essential micronutrient required in mitochondria and chloroplast reactions, enzyme systems related to photosystem II electron transport, cell wall lignification, carbohydrate metabolism, and protein synthesis (Verkleij & Schat, 1990). Zn is an essential micro-nutrient of numerous enzyme systems, respiration enzyme activators, and the biosynthesis of plant growth hormones (Ernst *et al*., 1992). Fe is the third important essential metal absorbed by *A. marina* an important component of chlorophyll, protein synthesis and root growth (Jones *et al.*, 1991). Moreover, oxygen released by the roots of mangrove plant creates an oxidant geochemical microenvironment (Silva *et al*., 1990), which helps to oxidize soluble Fe^{2+} and Mn^{2+} to insoluble $Fe(OH)_3$ and MnO_2.

Researchers have also highlighted that a higher concentration of Cu, Pb and Zn in the mangrove ecosystem results in significant reductions in seedling height, leaf number and root growth of some mangrove plants (MacFarlane & Burchett 2002). However, the overall health of *A. marina* plants in the study region was good. This is in conjunction with couple of previous studies in which no apparent impact on the health of mangrove tissues was observed despite metal accumulation in high concentrations (Gleason *et al*., 1979; Clough *et al*., 1983; Perdomo *et al*., 1998; MacFarlane & Burchett, 2001, 2002; MacFarlane *et al*., 2003). High degree of natural regeneration *A. marina* was reported in the present study, indicative of low impact of heavy metal on its morphology as it can be seen from the lsuh green and dense mangrove vegetation in few of the study sites (Figure 6). A similar significant observation was also made in a study carried out by Shete *et al*. (2007), wherein they reported luxuriant growth of *A. marina* in Ghatkopar area of Mumbai with high Pb concentration in the sediments. These observations further fortify the fact that *A. marina* is highly adaptable even under pollution conditions in the ecosystem.

Many different plants have been successfully established as hyperaccumulators of heavy metals, thereby playing an important role in the phytoremediation which requires effective translocation of pollutants from the roots to the shoots enabling harvest and removing of contaminants

Figure 6. Flourishing *A. marina* vegetation in Purna and Kolak estuaries**.**

(Kumar *et al*., 1995). Such hyper accumulators are not only tolerant to high concentration of pollutants in the system but also exhibit bio-concentration factor > 1 (Ma *et al*., 2001b; Baker & Whiting, 2002). However, in this study the BCF values for *A. marina* throughout the study sites was found to be low (almost negligible for non-essential heavy metals) with poor mobility across the different tissues. Thus, it can be concluded that *A. marina* cannot be categorized as hyperaccumulators. Considering the physiology of the plants that allow it to sustain high heavy metal content in the sediments, *A. marina* can be used for plantation programme in the contaminated soils for long term sustainable functioning of estuarine ecosystem.

Conclusion

The current study comes with an important finding that despite the high pollution levels in the estuaries of South Gujarat due to disposal of industrial effluents, *A. marina* has successfully adapted itself to this stress condition with a mechanism for selective uptake of only necessary minerals. Furthermore, the metal content in different plant parts clearly reveal that the movement of non-essential metals in the order pneumatophores > twigs > leaves is restricted. The movement of essential metals such as Zn and Cu has greater mobility upto leaves, where they are utilized for various biochemical processes. The bio-concentration factor for this plant was less than 1 and cannot be categorized as hyper accumulators. Considering the physiology of the plants that allow it to sustain high heavy metal content in the sediments, *A. marina* can be used for plantation programme in the contaminated soils for long term sustainable functioning of estuarine ecosystem.

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