STUDY ON HEAVY METAL CONTAMINATION OF PICHAVARAM MANGROVES

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ABSTRACT: This study is to collect the samples of true mangrove plant, associated mangrove plants, water and sediments from Pichavaram Mangrove Ecosystem and the samples are analyzed for heavy metals accumulation. Methods/ Statistical Analysis: The water, sediment and plant materials were collected at 6 locations. After the collection, the plant materials were washed with distilled water and they were dried and acid digested. Further the samples were subjected to analysis of heavy metals by flame atomic absorption spectrophotometer. Triplicate samples were analyzed and their results were expressed in ppm. The statistical analysis ANOVA (Analysis of Variance) and DMRT (Duncan Multiple Range Test) were used. Heavy metals contamination was observed in all samples. The mangroves accumulated more concentration than associated mangroves, therefore the Avicenna marina is suitable candidate for bio-accumulator and recommended for phytoremediation.

KEYWORDS: Accumulation, Ecosystem, Pichavaram, Heavy Metals, Mangroves, Phytoremediation.

INTRODUCTION
Mangroves are intertidal vegetation, thriving in the tropics and subtropics. They have a very high productivity and are sinks of nutrients and sediments. The mangroves ecosystems are characterized by high organic matter and low nutrient quality. They are estimated to cover an area of 1.7 to 2×10^5 km^2 across the world (Ramanathan et al., 2008). Mangroves play a significant role as sinks for anthropogenic contaminants and provide an important function in the coastal zones as buffer against erosion, storm surges etc. Mangroves are crucial for biogeochemical cycling of phosphorous, carbon and nitrogen. They have a huge microbial diversity and quite rich in invertebrates and other biota. They prevent erosion with their thick, extensive root system, by holding sediments together. These ecosystems provide an ideal site for studying a number of processes that are important in understanding hydro geochemical processes such as mixing, evaporation, dissolution and chemical exchanges between water and sediments (Ramanathan et al., 1998). They are the second highest source of primary production next to rainforest.(Singh et al., 2005). They provide high detritus and release nutrients, which are food source for various organism and provide home to variety of marine and terrestrial organisms. These important inter-tidal estuarine wetlands are exposed to anthropogenic contamination from tidal water, river water and land-based sources (Klekoski et al., 1994) as well to the natural calamities. As with most ecosystems, an intricate relationship exists between mankind and mangrove. They have several ecological, socio-economical, and physical functions that are essential in maintaining biodiversity and protecting human populations. Many indigenous coastal residents rely on mangroves to sustain their livelihood and traditional cultures. Mangroves are sustainably used for food production, medicines, fuel wood, fishery, honey and construction materials (Singh et al., 2005). Their complex architecture, combined with their location on the edge of land and sea, makes mangrove forests strategic greenbelts that provide a doubly protective system against natural calamities as well as provide sink for anthropogenic contaminants.

MATERIALS AND METHODS
Pichavaram Mangroves:-
The study site, the Pichavaram mangrove (Lat 11° 23' and Long 79° 47’), is located between the Vellar and Coleroon estuaries and has direct opening to the Bay of Bengal at Chinnavaikkal (Fig. 2.1). The area of the mangrove forest is 1100 ha, 50% covered by forest, 40% by water ways and rest filled by mud and sand flats (Krishnamurthy and Jayaseelan, 1983). It has 51 islets ranging in size from 10 m2 - 20 km2 separated by intricate waterways, that connects the Vellar and Coleroon estuaries. The southern part of the mangrove forest is dominated by mangrove vegetation, while northern part near the Vellar estuary is dominated by mud flats. The Pichavaram mangrove is influenced by mixing of the three types of waters (Kathiresan, 2000).
1. Neritic water from the adjacent Bay of Bengal through a mouth at Chinnavaikkal.
2. Brackish water from the Vellar and Coleroon estuaries and,
3. Fresh water from the irrigation canal (Khan Sahib Canal) as well as main channel of the Coleroon river.
The tides are semi-diurnal varying in amplitude from about 0.1 to 1 m in different regions during different seasons, reaching maximum during monsoon and post-monsoon and minimum during summer. The rise and fall
of the tidal waters is through a direct connection with the sea at Chinnavaikkal mouth and also through the two different estuaries, the Vellar and the Coleroon (Fig. 2). The depth of the water ways range from about 0.3 to 3 m.

**Geology:**
Since the Pichavaram mangrove ecosystem is lying between the rivers Vellar and Coleroon, therefore alluvium is dominant in the western part and fluvial marine and beach sand cover eastern part of the mangrove. Geomorphology of the area is majorly covered by floodplain, sedimentary plain and beach sand. Major part of the area falls under nearly level sloping category. The soil group of the area is Hydrological soil group `C' (USDA) low infiltration and moderate runoff potential found 50% area. The soil group `B' with moderate runoff is covering about 45% areas. The remaining 5% area is occupied by soil group `A' with high infiltration low runoff potential.

**Sample Preparation and Analysis**
Water Samples 25 ml of water samples were collected and filtered by using Whatmann No. 1 (0.45 μm) filter paper and the pH was adjusted to 3.5 with help of 0.1 N of HCl. Then the nitric acid digestion procedure was followed (APHA 2005). A blank was also digested using the de-ionized water as a reference material.

**Sediment Samples**
The collected soil samples were oven dried at 105°C and homogenized by using mortar and pestle according to normalize the grain size. Then the homogenized samples were subjected sieved through a 250 μm pore size and it was store in the plastic bottles for further study. Finally the sieved sediment samples were subjected to perchloric acid digestion Ramanibai et.al. (2012).

**Plant Samples**
The fresh plant materials like mature leaves, stems and roots were collected from selected mangrove species Avicennia marina and associated mangrove species Suaeda nudiflora and Sesuvium portulacastrum. The roots were carefully collected after removing the sediments. All the samples were labelled and stored in cool box with ice at 4°C and transported to the laboratory and the leaves bark and root samples were thoroughly clean the debris with glass distilled water and then allowed to oven dry at 60°C for 24 hours.

**Heavy Metal Analysis**
The acid digested triplicates samples were analyzed for heavy metals (Cr, Cu, Cd, Hg, Pb and Zn) accumulation by Atomic Absorption Spectrophotometer (AAS - Perkin-Elmer AA700)12 and the concentrations were expressed in ppm.

**Statistical Analysis**
Analysis of Variance (ANOVA) and Duncan Multiple Range Test (DMRT) were used to analysis of selected heavy metals. The differences of metal concentrations among the plant parts were studied. The statistical analyses were carried out through SPSS 15.0.

**RESULT AND DISCUSSION:**
Heavy metal contamination in the mangrove ecosystems is the matter of concern as its long persistence and continuous anthropogenic inputs.

**Temperature:**
The weather condition in the Pichavaram mangrove area is typical tropical climate. For the sake of convenience, the whole year is divided into 4 seasons: Post-monsoon (January–March), Summer (April – June), Pre-monsoon (July – September) and two Monsoons (south-west monsoon from June - July and north-east Monsoon October - January). Maximum and minimum temperature was ranged from 29 –36°C and 18.2 – 25°C respectively. The wide range of temperature fluctuations drives rapid changes in the daily and monthly mean humidity in the atmosphere along with the wind speed which may be one of the main factors controls the nutrient chemistry in this area.

**Rainfall:**
There is a wide fluctuation in total precipitation. Annual rainfall was 1463.9 ± 329.9 mm during 1998 – 99, and the number of rainy days was 53 ± 8.7 (Kathiresan 2000). About 75 – 90% of total rainfall was recorded during north – east monsoon (October – December).
accompanied by few depressions in the Bay of Bengal, while low rainfall was recorded in south – west monsoon (April – June).

Flora:-
The Pichavaram mangrove is one of the best example for best flora, both micro and macro. It has total of 22 species of sea weeds, of which 11 species belongs to green algae, 2 species to brown algae and the remaining 9 species belongs to red algae (Kannan and Thangaradjou 1998). It has also 22 species of blue – green algae (cyanophyceae; Krishnamurthy et al. 1995).

Fauna :-
The Pichavaram mangrove ecosystem is not only rich for floral diversity but also for faunal diversity. It harbours both invertebrate and vertebrates. The major invertebrate communities in this mangrove environment belongs to polychaetes, bivalves, gastropods, teneids, isopods, amphipods, cirripedes, crabs, shrimps and hermit crabs (Kathireshan, 2000).

Microbial diversity:-
The fertile status of the mangrove soils is controlled by the microbial flora in the mangrove sediments. High amount of microbial numbers was observed in the monsoonal days (Kathireshanet al., 1998). Among the microorganisms, the ratio between fungal and bacterial population was about 1:7000 (Krishnamurthy et al., 1987). In all, 52 species of bacteria and 23 species of fungi have been recorded.

Heavy metal (Fe, Mn, Cu, Pb, Zn) concentrations in Core sediments of Pichavaram Mangroves:

Iron:-
The concentration of iron varied from 7.756% to 4.49%, with an average value of 6.23%. Though concentration of iron shows an irregular trend but in general it decreases with increasing depth. Concentration of iron was found to be lowest (4.49%) at the depth of 30 cm and highest concentration (7.756%) was found to be at the depth of 15 cm (fig.2). Temporal variation shows increase in concentration with time i.e. in the depth sediments deposited in the past, Fe was much lower as compared to the recent sediments. The bottom layers having low concentration probably reflect the undisturbed and background concentration.

Manganese:-
The concentration of Mn varied between 422 mg/kg to 133 mg/kg with an average value of 277 mg/kg. Likewise the depth variation of Fe, concentration of Mn does not follow any regular trend but overall it decreases with depth.
At the depth of 17 cm the concentration is found to be highest (422 mg/kg) and at the depth between 19-22 cm there is significant decrease in concentration which may be attributed to processes like leaching, metal up-take by vegetation and post-depositional remobilization (Ramanathan et al., 1996) in the past which may have led to scavenging of Mn from the sediments thereby decreasing its concentration.

Temporal variation shows increase in concentration with time. The bottom layers having low concentration probably reflect the undisturbed and background concentration. Mn /Al ratio varied from 0.014 to 0.004. Overall Mn concentrations in core sediments are less than in the average shale (fig. 4) indicating Mn uptake or scavenging by various processes at most of the depths.

Copper:
The concentration of Cu varied between 55 mg/kg to 31 mg/kg and the average value was 43 mg/kg (fig. 5). Concentration of Cu though shows an erratic trend with increase and decrease at regular intervals but overall it fluctuates equally around the mean value. The highest concentration is found to be at the depth of 33.5 cm. Cu is mainly derived from the estuarine sediment or from the agricultural soil. The Al normalized Cu ratios were overall higher than the shale value indicating the sediment composition was different from the average continental shale composition with respect to Cu. The ratios were much higher at the depth of 8 cm and 33.5 cm

Lead:
The concentration of lead varied between 318 mg/kg to 180 mg/kg with an average value of 249 mg/kg. Concentration of lead remains almost constant with increasing depth with slight fluctuation at uppermost depths (fig. 8).
The highest concentration is at the depth of 8 cm (318 mg/kg). The recent sediments are found to be having high concentration of Pb as compared to the older deposited sediments which can be probably due to the increased sources in the recent past. Sources of Pb are both geogenic and anthropogenic. Anthropogenic sources may include the use of mechanized motorboats. Pichavaram being a tourist spot, the use of leaded diesel fueled motor boats as a mode of transportation is very prevalent in this area. In Pichavaram, increase in lead concentrations may be due to the direct input of nitrate compounds from external sources, largely from the aquaculture effluents, agricultural runoff and domestic sewage (Purvaja and Ramesh 2000; Subramanian 2004). Pb is derived from lead-bound paint industries, and input of effluents from the thermal power plants situated in the upstream of the estuary together with auto exhaust emission, atmospheric deposition and operation of a large number of mechanized fishing boats in the area (Settle and Petterson 1982; Nolting and Helder 1991).

**Zinc:**
The concentration of zinc varies between 163 to 115 mg/kg and the average value is 139 mg/kg. Concentration of zinc is almost constant with depth (fig. 4.9) with sudden increase at a depth of 35 cm (163 mg/kg). Sources of zinc include both geogenic and anthropogenic that includes aquaculture and agriculture.

**CONCLUSION:**
Mangrove forests are highly productive environment after the rain forests. It has been well documented that it provides number of ecological, educational and economic services to the human society. At the same time, it also controls the global biogeochemical cycles of nutrients and supplies considerable amounts of nutrients for the oceanic biological productivity. The mangrove environment is highly vulnerable not only to the natural hazards but also impacted by human disturbances. The
current project has been done on the trace metal geochemistry of Pichavaram mangrove sediments and following conclusion can be drawn out of the study. Fe is found to be the dominant metal in Pichavaram mangrove sediments. Temporal variation shows increase in concentration with time i.e. in the depth sediments deposited in the past, Fe was much lower as compared to the recent sediments. It can be inferred that Fe content has increased over time. Concentration of all the metals normalized with Al ratio for the core sediments was found to be quite higher than the shale metal/Al values (except for Mn) indicating concentration of metal in the Pichavaram core sediments were elevated with respect to average shale. Mn, however showed decreased Al normalized values which can be due to scavenging of Mn by various chemical and biological processes. Temporal variation of both Fe and Mn showed increase in concentration with time. The bottom layers having low concentration probably reflected the undisturbed and background concentration. The down core variation of Fe and Mn showed similar trend indicating similar geochemical behavior of the two metals in Pichavaram sediments. The depth variation of other metals like Cu, Pb and Zn was practically constant and fluctuated more or less equally from the average values. Pb however showed higher values in the upper sediment indicating recent deposition.

In the present work, Geoaccumulation index for majority of metals was smaller than 0 at all the depths showing practically no contamination and consequently no or negligible anthropogenic input. Igeo was significant only in the case of Pb. Enrichment factor of various trace metals was evident in case of all the metals. Anthropogenic factor for all metal validates the existence of contamination. Contamination factor is highest in case of lead and it is lowest in case of Copper. With the help of contamination factors of all metals, pollution load index was calculated which was 2.49 showing the pollution level of trace metals validating the presence of contamination and anthropogenic interferences in Pichavaram Mangroves. The study overall reveals that there are possible sources of pollution and contamination in the Pichavaram Mangroves and pollution load index is 2.31 indicating that there is a moderate contamination prevailing over Pichavaram Mangroves.

REFERENCES:-