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Bioaccumulation of Heavy Metals Pollutants in Pichavaram Mangrove Ecosystem, Southeast Coast of India

Anbu Annamalai

Biodiversity and GIS Lab, Department of Environmental Sciences

Bharathiar University, Coimbatore, Tamil Nadu, India

Present address: Tamil Nadu Forest Department, Kalakad Mundandhurai Tiger Reserve

Manoj Kaliyappan

Present address: Tamil Nadu Forest Academy, Coimbatore, Tamil Nadu

Manimekalan Arunachalam (Corresponding Author)

[1]Biodiversity and GIS Lab, Department of Environmental Sciences, Bharathiar University

Coimbatore, Tamil Nadu, India. E-mail: manimekalan@buc.edu.in

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Abstract

Studies on contaminant bioaccumulation in tropical mangrove ecosystems are very limited. An attempt has been made to assess sources of primary productivity and chemical bioaccumulation behavior in true and associated mangrove plants, water, and sediments from the Pichavaram Mangrove Ecosystem. The water, sediment, and plant materials were collected at 7 different locations and the samples were analyzed to determine the concentration of heavy metals using a flame atomic absorption spectrophotometer. The result reviles that the maximum lead concentrations of 5.48 ppm/g were accumulated in sediment samples collected from shrimp pond effluent and 4.26 ppm/l from water during post-monsoon. The maximum Zinc concentration of 12.34 ppm/g was observed in sediment samples collected from degraded mangrove forests during post-monsoon and 10.99 ppm/g was observed in sediment samples during the summer season. Higher heavy metals concentration was observed during spring and summer this may be due to increased biological activities, land runoff and rainfall during these seasons. The maximum Copper concentration 9.07 ppm/g was observed in sediment at degraded mangrove forest during post-monsoon and 8.16 ppm/g was observed in sediment during the summer season. Heavy metals concentrations in different parts of *A. marina* mangrove plants were analyzed. In leaf sample, Pb 5.44 ppm/g in shrimp pond effluent site, Cd 4.97 ppm/g in degraded site, Zn 4.43 ppm/g in degrading site, Cr 2.17 ppm/g in Freshwater zone at Vellar, Hg 1.68 ppm/g in shrimp pond effluent site, Cu 0.86 ppm/g in Freshwater zone at Upannar was recorded. In stem sample Pb 6.89 ppm/g and Zn 5.67 ppm/g in the degraded site, Cd 5.27 ppm/g in the natural site, Hg 4.91 ppm/g in degrading, Cr 2.49 ppm/g and Cu 0.87 ppm/g in Freshwater zone at Upannar was recorded. In *Avicennia* roots, Cr 10.89 ppm/g in shrimp pond effluent, Pb 10.17 ppm/g in natural site, Cd 6.89 ppm/g in freshwater zone at Vellar, Zn 6.86 ppm/g in degrading mangrove site, Hg 5.48 ppm/g in degraded site, Cu 0.92 ppm/g in backwater mouth was recorded. Heavy metals contamination was observed in almost all the samples in higher concentrations. The results indicate that *Avicennia marina* have a greater potential to observe and accumulate higher concentration than associated mangroves. *A. marina* plant can be used for phytoremediation to remove the heavy metals from the mangrove ecosystem and will help for ecological studies, conservation and sustainable management of the mangrove habitats.

Keywords: Contaminant, water, sediments, *Avicennia*, Zinc, Copper, Upannar, Phytoremediation, Mercury

1. Introduction

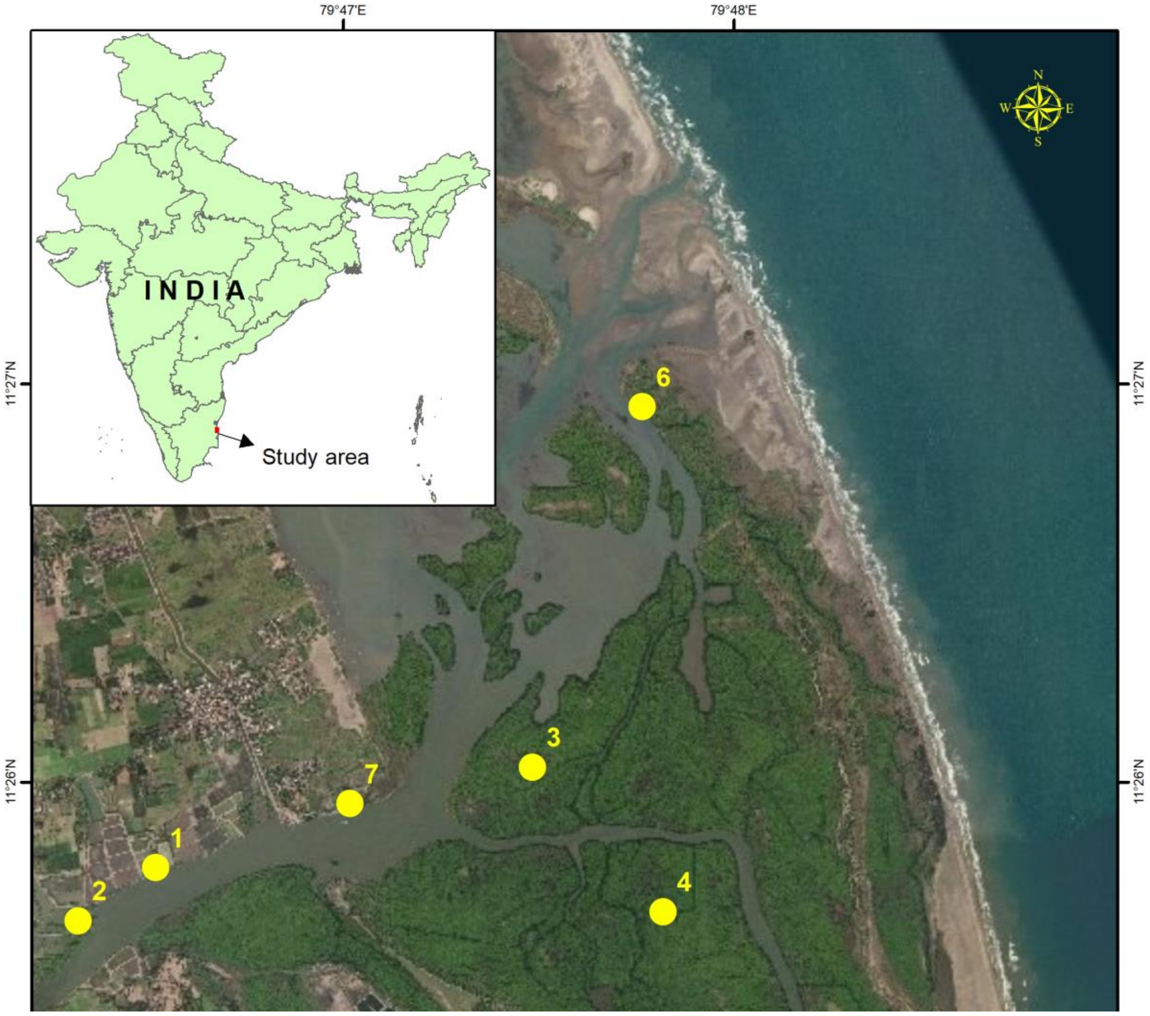
Mangroves are the only woody plants that grow at the interface between land and sea in tropical and sub-tropical latitudes, where they exist in high salinity, extreme tides, strong winds, high temperatures and muddy, anaerobic soils. There may be no other group of plants with such highly developed morphological and physiological adaptations to extreme conditions. Mangrove forests, the world's most productive ecosystems that enrich the coastal waters, protect coastlines and enrich coastal waters with a yield of diversified commercial forest products, protect coastlines, and support coastal fisheries (Kathiresan and Bingham, 2001). The mangrove ecosystem plays an important role in providing goods and services to humans, which includes aquaculture, forestry, shoreline protection from erosion, burning wood and household materials and other products like honey, wax and essence (Walters et al., 2008). Further Mangroves ecosystem helps in addressing climate change issues by sequestration of atmospheric carbon. It act as bioshield by reducing wind velocity during cyclone, tsunami and so on. At present manmade activities like shrimp aquaculture, usage of chemical fertilizers, pesticides and heavy metal pollution from upstream are threatening the coastal and also the mangrove ecosystems. The mangrove forests are exposed to heavy metal pollution due to mining, metal smelting, burning of fossil fuels and agricultural pesticide production and as well as domestic and industrial sewage. These are harmful to microbes and humans by affecting the food chain (Pahalawattaarachchi *et al.*, 2009). The mangroves sediments have a high affinity towards metal binding due to its lavishness of sulfide content to attach easily and they are anaerobic nature, which can undoubtedly get the metals and increment the grouping of metals in the mangrove silt, along these lines this accessibility of metal focus prompts bioaccumulation in both plant and animal tissues (MacFarlane *et al.*, 2003). However heavy metal pollution can damage both the biodiversity and ecosystem through the tendency of bioaccumulation in the food chain of marine biota. More than three decades of the world's human population lives in coastal watersheds (Vitousek *et al.*, 1997). Not surprisingly, the amounts, types and ecological impacts of pollutants discharged to estuarine and coastal waters are closely linked to population growth in these watersheds (Peierls *et al.*, 1991; Nixon, 1995).

However, the heavy metal pollution can damage both biodiversity and ecosystem through the tendency of bioaccumulation in the food chain of marine biota. The heavy metal bioaccumulation is directly proportional to the concentration of metals in the surrounding environment like water, sediments and period of time exposure, in addition other factors like salinity, pH, hardness and temperature are responsible for accumulation (Blackmore and Wang, 2002). The mangrove wetlands are frequently subjected to heavy metal pollution by anthropogenic sources because they are located intertidal areas of coastal region (Abohassan, 2013). Mangroves have ability to tolerate high levels of heavy metals (MacFarlane *et al.*, 2007) particularly the *Avicennia* species have capacity to accumulate more amount of heavy metals than other mangrove species (MacFarlane and Burchett, 2002). The heavy metals pollution in the coastal area and its bordering ecosystem of mangroves are subjected to serious threat for environmental safety (Chakraborty *et al.*, 2014). Numerous studies revealed that the accumulation potential of heavy metals in water, sediment and commercial faunal species but heavy metals accumulation studies of mangroves and associated mangroves species of Pichavaram Mangrove Ecosystem are rare. Therefore, an attempt was made to understand the bioaccumulation potentials of mangrove species like *Avicenia marina* and associated mangrove species *Sesuvium portulacastrum* and *Suaeda nudiflora* were collected from Pichavaram Mangrove Ecosystem. This study was carriedout to analyse the heavy metals like Cr, Cu, Cd, Hg, Pb, and Zn in the sediments, water and leaves, stems and roots of *Avicenia marina*, *Sesuvium portulacastrum* and *Suaeda nudiflora* to understand the bioaccumulation potentials and its ecological management of the Pichavaram Mangrove Ecosystems.

2. Materials and Methods

2.1. Study Area and Sampling Stations

This study was carriedout in Pichavaram mangrove forest which is located between 11˚20' N and 79˚ 47' E in the Vellar and Coleroon estuaries, near Chidambaram, Tamilnadu (Map 1). The mangrove covers an area of about 1100 ha, of which 50% is covered by forest, 40% by water-ways and the remaining filled by sand-flats and mud-flats (Krishnamurthy and Prince Jayaseelan, 1983). The Pichavaram mangrove is influenced by mixing of three types of waters: 1. Neritic or costal water from Bay of Bengal through a mouth called 'Chinnavaikkal', 2. brackish water from the Vellar and Coleroon estuaries and 3. fresh water from an irrigation channel (Khan Sahib canal'), as well as from the main channel of the Coleroon river.



Map 1. Map showing the study area and sample collection location

Seven sampling stations were fixed along the Pichavaram Mangrove forest. The sampling locations were selected based on the properties of physicochemical parameters and the source of contaminations. The water, sediment and plant samples were collected from seven different locations of the Pichavaram Mangrove forest during Post monsoon (February, 2018) and Summer (May, 2018) 1.Shrimp Pond effluent site (N 11^0 25'14.4", E079^0 45'56.9"), 2. Degraded Mangrove site (N 11^0 25'54.9", E079^0 47'18.3"), 3. Natural site (N 11^0 25'45.6", E079^0 47'43.2"), 4. Barren site (N 11^0 25'56.7", E079^0 47'05.9"), 5. Freshwater Zone – Uppanar (N 11^0 25'41.1", E079^0 46'15.7") and 6. Vellar (N 11^0 25'04.2", E079^0 46'19.5") and 7. Backwater Zone – Mouth (N 11^0 27'13.1", E079^0 47'40.1"). The details of the study area in given in Table 1.

2.2. Sample Preparation and Analysis

2.2.1. Water Samples

25 ml of estuarine 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 standard.

2.2.2. Sediment Samples

The collected sediment samples were oven dried at 105ºC and homogenized by using mortar and pestle to normalize the grain size. Then the homogenized samples were subjected to sieve and pass through a 250 µm pore size and it was stored in sterile plastic containers for further study. Finally, the sieved sediment samples were digested using perchloric acid for heavy metal analysis (Ramanibai, 2012).

2.2.3. Plant Samples

Mature leaves, stems and root samples were collected from *Avicennia marina* and associated mangrove species *Suaeda nudiflora* and *Sesuvium portulacastrum*. Leaves, bark and root samples were thoroughly washed with running tap water to remove the debris and then with double distilled water and it was oven dried at 60°C for 24 hrs (Agoramoorthy, 2009). All the collected samples were labeled and stored in icebox at 4°C and transported to the laboratory immediately for further analysis.

2.2.4. Heavy Metal Analysis

The acid digested triplicates samples were analyzed for heavy metals (Cr, Cu, Cd, Hg, Pb and Zn) by using Atomic Absorption Spectrophotometer (AAS - Perkin-Elmer AA700).

3. Results

In seven stations the distribution of mangroves were dominant in natural site *viz., Avicennia marina, Rhizophora mucornata, Rhizophora apiculata, Ceriops decandra, Bruguiera cylindrica, Aegiceras corniculatum, Lumnitzera racemosa and Suaeda* followed by Freshwater Zone – Uppanar, Freshwate Zone-Vellar and Backwater Zone – Mouth. The minimum was recorded in Shrimp Pond effluent site that consist of only *Suaeda martima* species.

The soil and water samples were analyzed for pH, TDS and temperature from 7 different sites during post monsoon and summer season and the physico-chemical parameters, number of crab holes, sediment analysis, soil moisture and nutrient levels were shown in Table (2 -5). The maximum pH, salinity and temperature was found during post monsoon seasons compared to summer seasons. The pH ranges between 8.4 (site 6) and 8.1 (site 2 & 5) during monsoon, 8.5 (site 6) and 8.3 (site 5) during post monsoon season. The salinity was maximum found in post monsoon seasons at 49 ppt in site 3 and minimum in summer season at 11 ppt (site 6). The water temperature was maximum found in post monsoon seasons(January - February) at 31˚C in site 2 and minimum in summer season(March-May) at 22˚C (site 4). The soil temperature was maximum found in post monsoon seasons at 35˚C in site 2 and minimum in summer season at 24˚C (site 3). The crab hole was counted by measuring 1m x 1m and the number of crab holes were taken into consideration for determining the wealth of mangrove ecosystems (Navodha Dissanayake and Upali

Chandrasekara, 2014). Sediment characteristics like sand, silt and clay were studied for their composition and it varies according to the sampling site. The soil wet and dry weight was also measured for their water holding capacity in mangrove environment. Micronutrients like Nitrogen, Phosphorous and Potassium were studied for their levels. Among these Nitrogen levels, the natural site was found to be very higher than any other stations in all the two seasons.

Heavy metals concentrations of sediments and water samples were represented (Fig.1 a & b). The concentration of lead in water was highest in station 1 (4.26 ppm) while the concentration of the following metals like mercury (1.12 ppm), iron (0.07 ppm) and Arsenic (2.18 ppm) were highest in the same station 1 except the concentration of copper, it was high in station 5 (0.01 ppm) during monsoon season. In post monsoon season the concentration of heavy metal accumulation in the water samples were mercury (1.08 ppm), iron (0.04 ppm), lead (4.05 ppm) and Arsenic (2.10 ppm) in station shrimp pond effluent site of Pichavaram Mangrove Ecosystem. In water samples, most of the metals and its concentration were accumulated in high concentration during monsoon season. However, in the sediments, the concentration of iron (340.97 ppm), zinc (12.34) and copper (9.07) was highest in degraded site during summer seasons. The concentration of magnesium (38.82 ppm) is high in station 5 than Manganese (17.20) in station 6. The metals like mercury (4.48 ppm), lead (5.48 ppm), arsenic (3.34 ppm) and cadmium (1.99 ppm) were also high in station 1. The heavy metal concentration was maximum in summer seasons (Fig. 2a & b) compared to post monsoon season, the low metal concentration is totally depending upon the fresh water inflow through rainfall and high concentration depends upon the evaporation of water by solar energy.

Heavy metal concentration of the *Avicennia marina* plant parts collected from the Pichavaram Mangrove forest were analysed in leaf, stem and root samples were shown in the Fig. 3 (a, b & c). Among the six metals tested for of *A. marina* plant parts from Pichavaram Mangrove Ecosystem, the accumulation of lead (Pb) concentration in the leaf was found highest in degraded mangrove site (5.44 ppm/g), minimum in back water mouth (BWM) (2.14 ppm/g) and Zinc (Zn) (4.43 ppm/g) maximum recorded in degraded site followed by BWM (3.10 ppm/g). The accumulation of Cadmium (Cd) (4.97 ppm/g) is found in degraded site, while minimum seen in (3.83 ppm/g in Shrimp pond effluent site). In Chromium (Cr) (2.17 ppm/g) found in Fresh Water Zone in Vellar (FWZ-V), minimum in 1.48 ppm/g in BWM site. Mercury (Hg) (1.68 ppm/g) recorded in Shrimp pond effluent site and minimum recorded in BWM (1.09 ppm/g). Copper (Cu) (0.86 ppm/g) in FWZ-Upannar, lower in shrimp pond site (0.61 ppm/g) respectively. Stem found that lead concentration was the highest (6.89 ppm/g) in degraded mangrove site and Zinc (5.67 ppm/g) in degraded mangrove site followed by Mercury (4.91 ppm/g) in degraded mangrove site, Cadmium (5.47 ppm/g) in FWZ-V, Chromium (2.49 ppm/g) in FWZ-U, and Copper (0.87 ppm/g) in FWZ-U, respectively.

In root samples, the concentration of lead was high (10.17 ppm/g – Natural site) and Chromium (10.89 ppm/g – Shrimp pond effluent) followed by Zinc (6.86 ppm/g – degraded site), Cadmium (6.89 ppm/g – BWM-V), Mercury (5.48 ppm/g – degraded site) and Copper (0.92 ppm/g - BWM), respectively. The Pb, Zn and Cu concentrations of *A. marina* roots were ranged in the following order (4.44 ppm to 10.17 ppm, 3.17 ppm to 6.86 ppm and 0.48

ppm to 0.92 ppm), stem of same species were ranged (3.17 ppm to 6.89 ppm, 3.14 ppm to 5.67 ppm and 0.58 ppm to 0.87) and leaf of *A.marina*, the concentration were ranged (2.14 ppm to 5.44 ppm, 3.10 ppm to 4.43 ppm and 0.61 ppm to 0.86 ppm). However, the *Sesuvium portulacastrum* and *Suaeda nudiflora* showed traces in accumulating the heavy metals. In compare to other halophytes mangrove species, the *A. marina* showed higher accumulation of the heavy metals. The following concentration of heavy metals accumulated in the plant parts of *A. marina*, that is Cr > Pb > Cd > Zn > Hg > Cu.

Table 1. Details of the plots studied in Pichavaram

Stations	Location of site	Latitude and Longitude	Dominant Mangrove species
1	Shrimp Pond effluent site	N 11^0 25'14.4", E 79^0 45'56.9"	*Suaeda martima,Sesuvium portulacastrum*
2	Degraded Mangrove site	N 11^0 25'54.9", E 79^0 47'18.3"	*Suaeda* species were found and starts to degrade. *Avicennia marina* were predominantly found in the creeks
3	Natural site	N 11^0 25'45.6", E 79^0 47'43.2"	*Rhizophora mucornata, Ceriops decandra, Bruguiera cylindrica, Aegiceras corniculatum, Lumnitzera racemosa and Suaeda*
4	Freshwater Zone - Uppanar	N 11^0 25'41.1", E 79^0 46'15.7"	*Rhizophora mucornata, Rhizophora apiculata, Avicennia marina*
5	Freshwate Zone-Vellar	N 11^0 25'04.2", E 79^0 46'19.5"	*Rhizophora mucornata, Rhizophora apiculata, Avicennia marina*
6	Backwater Zone – Nearby Mouth	N 11^0 27'13.1", E 79^0 47'40.1"	*Rhizophora mucornata, Rhizophora apiculata, Avicennia marina*
7	Barren site	N 11^0 25'56.7", E 79^0 47'05.9"	

Table 2. Analysis of crab holes, pH, salinity and temperature

Stations	No. of crab holes (1m x 1m)		pH		Salinity (ppt)		Temperature (°C)			
							Water		Sediment	
	Monsoon	Post monsoon	Monsoon	Post monsoon	Monsoon	Post monsoon	Monsoon	Post monsoon	Monsoon	Post monsoon
1.	12	19	6.9	7.1	18	20	29	30	31	32
2.	27	18	8.1	8.2	35	38	29	31	35	35
3.	53	63	7.6	7.8	48	49	24	26	24	28
4.	0	0	7.9	8.0	30	32	22	24	29	30
5.	21	28	8.1	8.3	15	18	24	27	26	28
6.	14	17	8.4	8.5	11	13	25	27	26	27
7.	9	16	7.7	7.9	40	41	26	29	27	28

Table 3. Sediment analysis

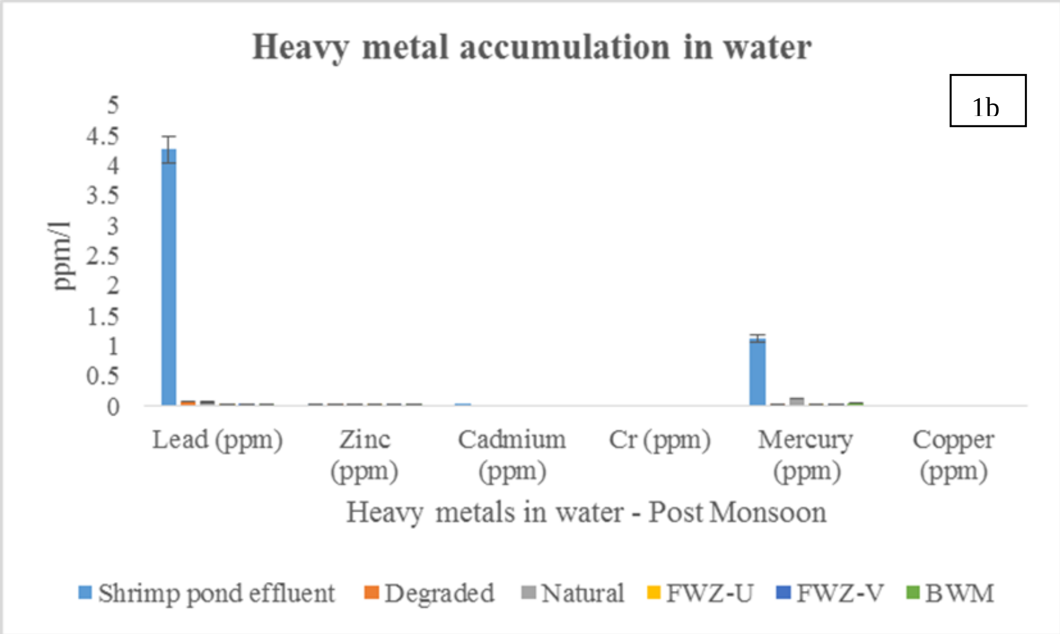
	Sand		Silt		Clay	
	Post monsoon	Summer	Post monsoon	Summer	Post monsoon	Summer
1	29.83	28.94	59.43	58.46	10.74	12.60
2	49.70	48.23	43.33	42.74	6.97	9.03
3	28.16	27.65	49.27	48.02	22.57	24.33
4	68.23	67.34	31.04	28.94	0.73	3.72
5	43.56	42.84	45.23	44.73	11.21	11.93
6	44.45	43.95	44.12	43.01	11.43	13.04
7	44.68	43.58	39.26	38.73	16.06	17.69

Table 4. Soil moisture (% of wet wt) at different stations

Station	Soil moisture (%)	
	Post monsoon	Summer
1	52.17	49.63
2	61.46	57.20
3	56.34	52.86
4	18.66	14.09
5	53.17	49.85
6	44.39	41.60
7	14.62	12.03

Table 5. Nutrient level at different stations

Station	Available Nitrogen (kg/ha)		Available Phosphorous (kg/ha)		Available Potassium (kg/ha)	
	Post monsoon	Summer	Post monsoon	Summer	Post monsoon	Summer
1	171.67	143.60	34.15	32.66	72.23	69.38
2	98.19	98.05	21.38	28.49	36.03	36.78
3	289.46	219.69	61.41	69.03	124.27	121.47
4	224.24	196.32	22.42	20.99	68.94	66.83
5	187.66	164.77	36.28	33.58	114.76	111.66
6	194.80	177.48	35.43	32.46	116.87	112.94
7	0	0	0	0	0	0



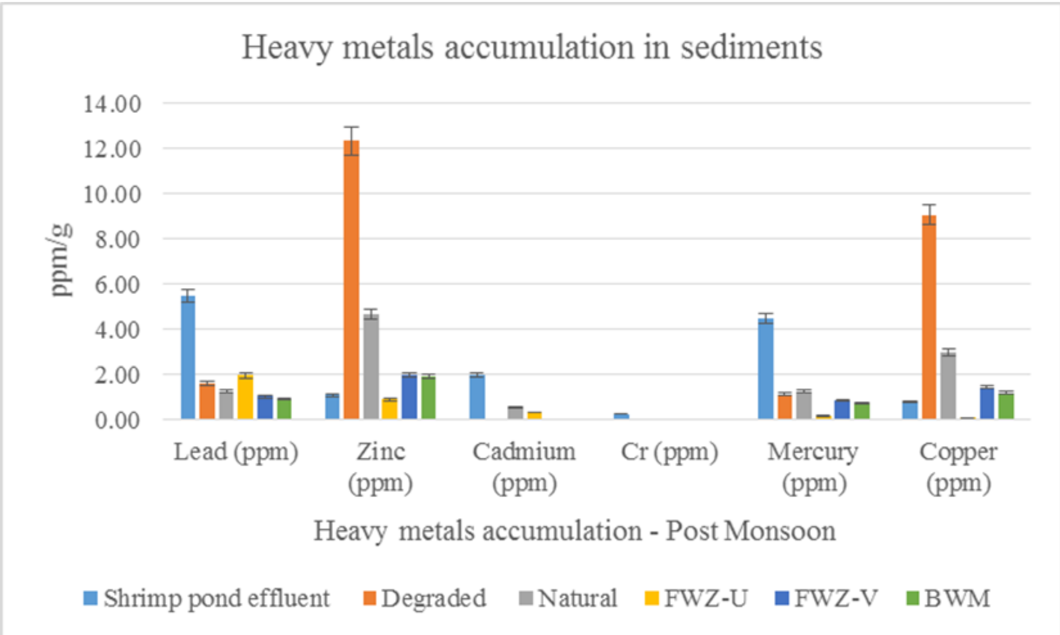
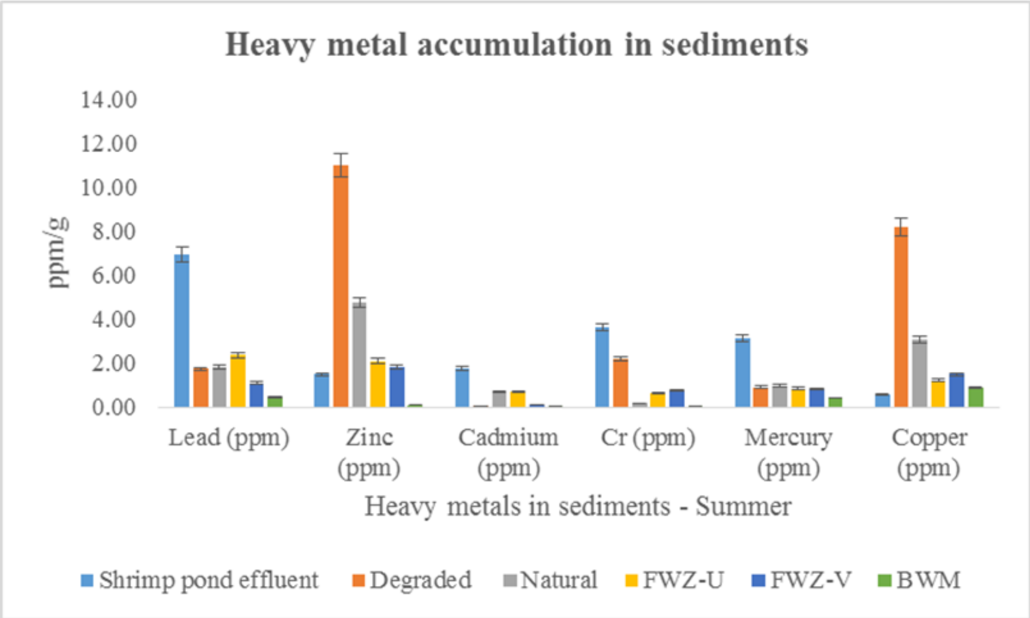


Figure 1. (a&b) Heavy metal data analysis in sediments and water from Pichavaram Mangrove Forest – Post Monsoon



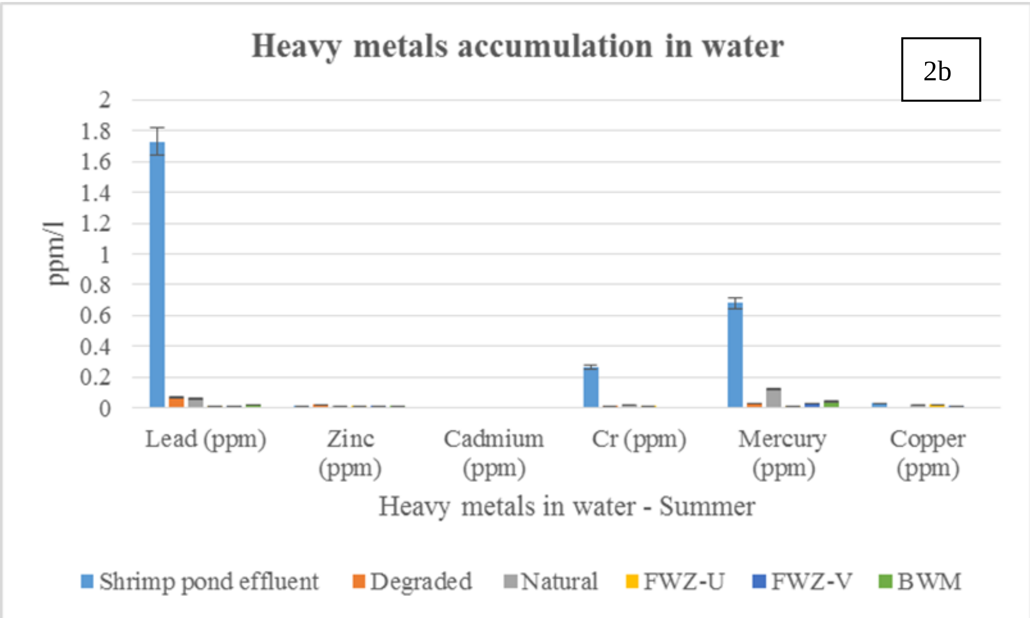


Figure 2. (a&b) Heavy metal data analysis in sediments and water from Pichavaram Mangrove Forest – Summer

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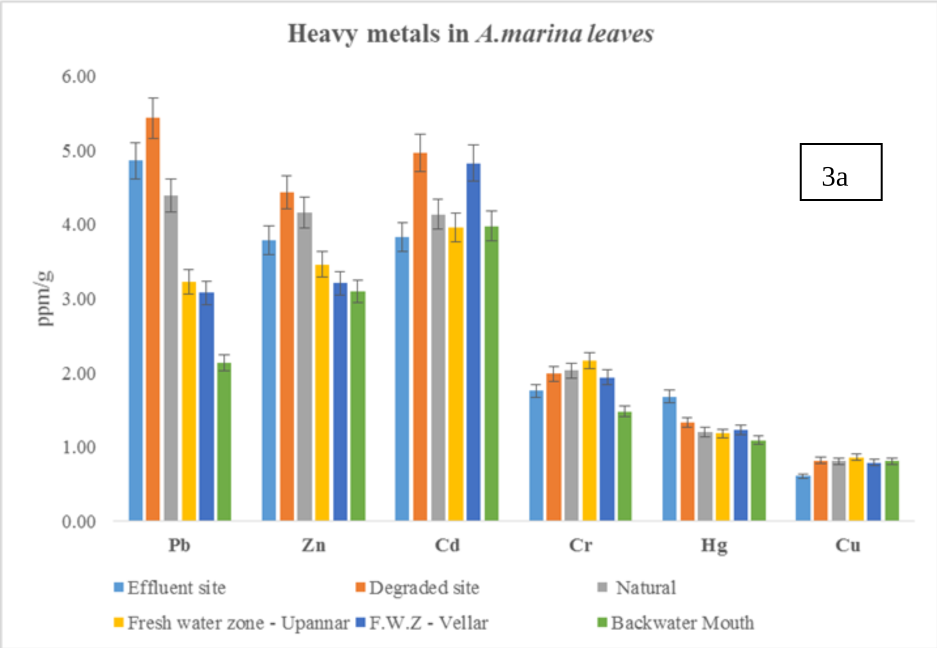

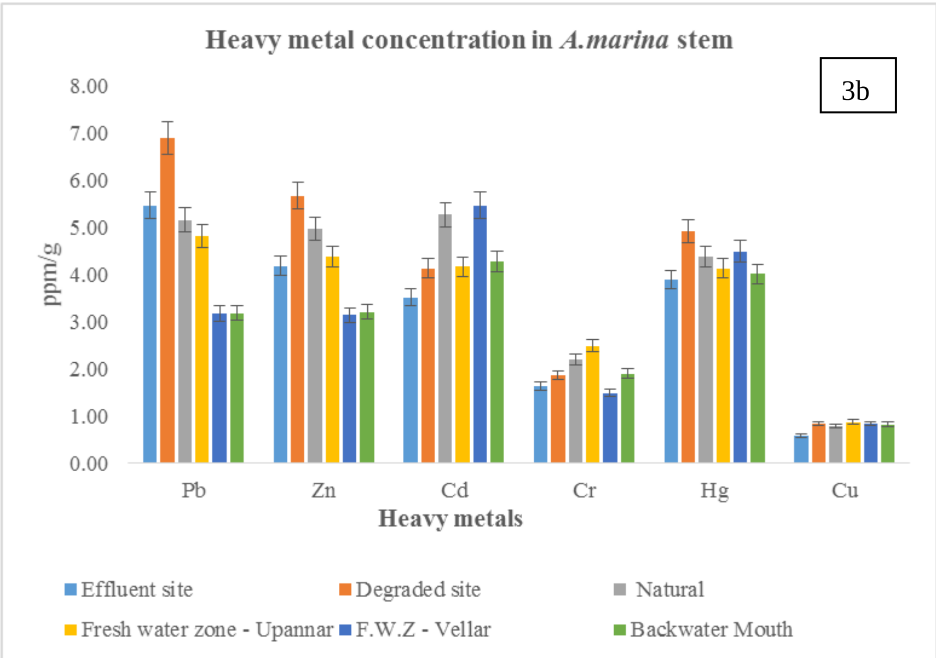

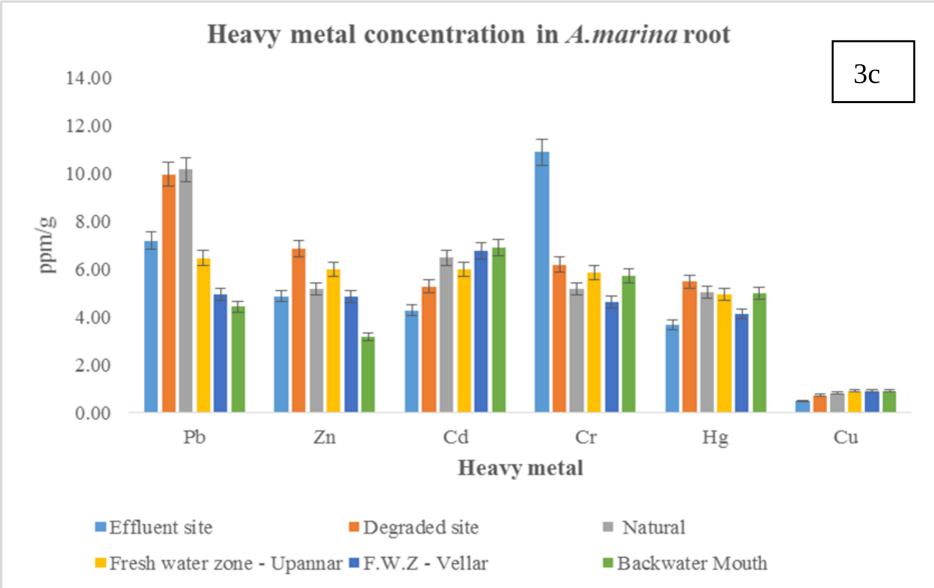

Figure 3. (a, b & c) Heavy metal data accumulation in plant parts of *A. marina*

4. Discussion

Throughout the study period, the pH, salinity and temperature values are found within the permissible limits in Pichavaram mangrove forest. The pH values were found to be 7.1 to 8.5 and higher during post monsoon season. In generally agreed that the pH of a stream must not be less than pH 4.5 and not more than 9.5 if fish are to survive (Harrison, 1990). Generally, fluctuations in pH values during different seasons of the year is attributed to factors like removal of by photosynthesis through bicarbonate degradation, dilution of seawater by freshwater influx, low primary productivity, reduction of salinity and temperature and decomposition of organic materials as stated by Karuppasamy and Perumal, 2000; Rajasegar, 2003. The salinity is the main physical parameter that can be attributed to the plankton diversity act as a limiting factor which influences the distribution of planktonic community (Balasubramanian and Kannan, 2005; Sridhar *et al.*, 2006). Generally, changes in the salinity of the brackish water habitats such as estuaries, backwaters and mangrove are due to the influx of freshwater from land run off, caused by monsoon or by tidal variations. During the monsoon season, the heavy rainfall and the resultant freshwater inflow from the land in turn moderately reduced the salinity. Thus the variations in salinity in the study sites were mainly influenced by the rainfall and entry of freshwater as reported earlier by Vijayalaksmi et al. (1993) in the Gulf of Kachchh; Saisastry and Chandramohan (1990) in the Godavari estuary and Chakraborty et al. (1990) in the Bay of Bengal.

The maximum concentrations of lead (4.26 ppm), Arsenic (2.18 ppm), mercury (1.12 ppm) and iron (0.07 ppm) in water and Iron (340.97 ppm), zinc (12.34 ppm) and copper (9.07 ppm) in sediment were observed during monsoon may be due to the settlement of heavy metals from the domestic and industrial waste water and solid waste. Mercury (4.48 ppm) concentration in sediment was higher during monsoon. Sediments can accumulate large quantities of chemicals particularly poorly soluble organic compounds that may be taken up by fish, both through contact with sediment and interstitial water and from food (Vigano, 2001). Sediment associated chemicals may or may not be bioavailable and there is a paucity of information on their combined effects on exposed organisms (Werner, 2004). The introduction of heavy metals, in various forms in the environment can produce considerable modifications of the aquatic communities and their activities. Migration of these contaminants into non contaminated areas as dust or leachates through the soil and spreading of heavy metals containing sewage sludge are a few examples of events contributing towards contamination of the ecosystems (Gaur, 2004).

Considerably Pb, Zn, Cd, Cr, Hg and Cu concentrations of the heavy metals were high in the mangrove root. Hence the mangroves plays an important role for reducing the heavy metals transport to the adjacent ecosystems like estuarine and marine ecosystems, since it acts as a sinks for heavy metals and also it have a tendency for immobilize the metals (Chakraborty *et* al., 2013).

Comparison of leaf and stem samples of *A. marina*, the roots accumulated high concentration of heavy metals in all the sites. The higher amount of heavy metal accumulation was recorded at degraded mangrove site followed by Shrimp pond effluent, FWZ-U, FWZ-V, natural and BWM of *A. marina* from Pichavaram Mangrove Ecosystem. Since, Plants have universal protective mechanism of stress particularly in the metals accumulation (Kamalraj *et al.*, 2008). Bioaccumulations of heavy metals in mangrove tissues are provided one of the indicators and used to monitoring the coastal heavy metals pollution in tropical and subtropical region (Saenger and McConchie, 2004).

5. Conclusion

Heavy metal concentration of the *Avicennia marina, Sesuvium portulacastrum* and *Suaeda nudiflora* plant parts such as leaf, stem and root were analysed in Pichavaram Mangrove ecosystem. The halophytic mangrove species, *A. marina* showed higher accumulation of the heavy metals in the following order as Cr > Pb > Cd > Zn > Hg > Cu. *Sesuvium portulacastrum* and *Suaeda nudiflora* showed traces in accumulating the heavy metals. The findings from the present study revealed that maximum concentration of heavy metals accumulated in the following root > stem > leaf of *A. marina*.

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