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# DETERMINATION OF HEAVY METAL CONCENTRATION (Cd, Cu, Cr, Pb) IN LEACHATE, SURFACE WATER AND FLOATING VEGETATION (EICHORNIA CRASSIPES (C. MART.) SOLMS (1883) SAMPLES AND ITS BIOREMEDIATOIN EFFICACY (TRANSPORTATION INDEX (Ti) AND BIOCONCENTRATION FACTOR (BCF)) IN PALLIKARANAI MARSH, CHENNAI, INDIA

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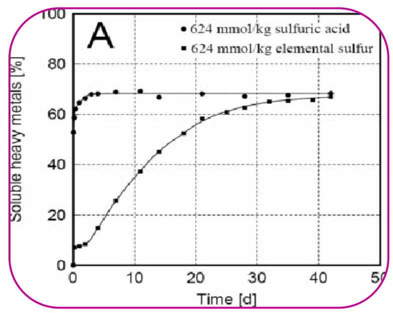
## ABSTRACT

*The current study aims at assessing the ecological condition of the wetland and provides bioremediation solution. The objective is achieved byassessing the heavy metal concentration (Cd, Cr, Cu, Pb) in leachate, water, as well as the floating vegetation (Eichhorneacrassipes) samples, the transportation index and the Bio-concentration factor of heavy metals in Eichorneacrassipes. Of these four heavy metals Pb is found to be the highest and Cadmium (Cd) to be the least accumulated in the study area. The Transportation index (Ti) reveals the capacity of the plant to transfer the heavy metals from root to the leaf. The studied species Eichhorniacrassipesis found to beshowing higher transportation index (Ti) for Cr and Pb with both showing more than 1 and Cu with 0.44 mg/kg. The Bio-concentration of Cr is found to be the highest in the target species followed by Pb to a greater extent showing its efficiency to bio accumulate chromium and lead and facilitate the process of phytoremediation.*




**KEY WORD:** *Eichorniacrassipes, Pallikaranai marshland, Heavy metals, AAS, Perungudi dumpsite, BCF, Ti*

## INTRODUCTION

Wetlands act as the reservoir for diverse species and sustain a complex and important food web. While it is obvious that wetlands provide vital support for the diverse fauna and flora to breed and feed, their mere existence now is under stake due to swelling pollution and negligence (Patnaik D, 2014). One such pollutants are Heavy Metals which are demarcated as metallic elements that have a comparatively higher concentration(more than 4g/cm3) and are toxic and lethal in low concentrations (Karen, 2005), and in this way, they inflict a major harm to the public health and to the environment because of their toxicity to many life forms including human being. Heavy metals find their way into the environment in two ways; through natural means and through man maid sources. Weathering of minerals, the eruption erosion of volcano are the major natural means. The antropgenin sources are smilting, mining, electroplating, use of fertilizers (posphates), pesticides and bio-solids as well in farm land, industrial effluents, atmospheric emission (Wuana and Okieimen, 2011).

## PHYTOREMEDIATION:

Phytoremediation used for removing heavy metal pollutants or reducing their toxicity using the plants and associated microbes (Bernal *et al.* 2005) is observed to be greatly efficient and beneficial. The intake of heavy metal contaminated food items has been recorded to be 20-40 times more than the estimation in the contaminated water (Foran,1990). The significant reason could be that the aquatic organisms possess the ability to accumulate heavy metals up to 105 times the heavy metal contamination in the water. (Guimaraes*et al*. 1985).Water hyacinth systems have also been reported to be very proficient in eliminating pollution from wastewaters and nitrogen elimination efficiency ranges from 10-90 % (U.S. EPA.1988).

## MATERIALS AND METHODS

**Figure 1: Study area**

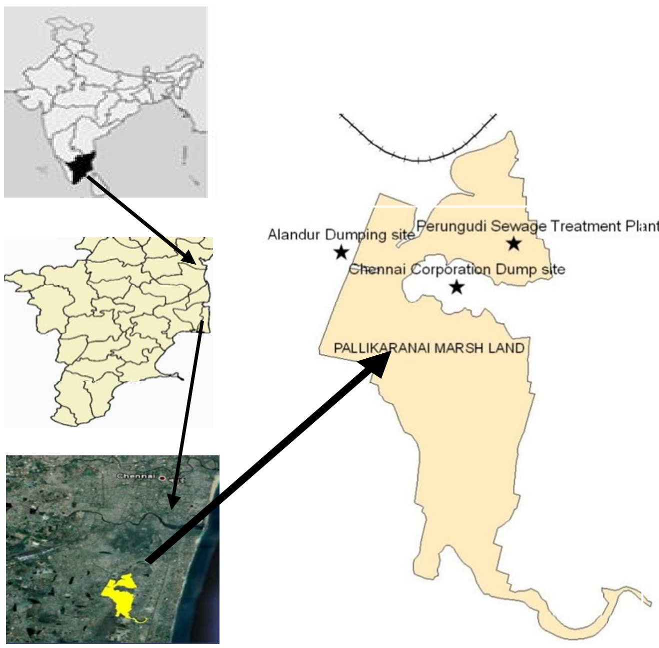



**Figure 2 : Study sites**


**Table 1 :GPS co-ordinates**

| SAMLING SITE | SAMPLE | LATITUDE | LAONGITUDE |
|---|---|---|---|
| 1 | P1 | 12°56’54.59’’N | 80°12’52.49’’E |
| 2 | P2 | 12°56’56.01’’N | 80°12’56.58’’E |
| 3 | P3 | 12°56’55.44’’N | 80°13’3.91’’E |
| 4 | P4 | 12°56’58.04’’N | 80°13’15.74’’E |

## STUDY SITE DESCRIPTION AND SAMPLE COLLECTION

Pallikaranai marshland, located in Kanchipuram district of Tamilnadu is a suburb of Chennai situated about 10 km from Adyar. The dump site of Perungudi is located at the northern region of a wide low lying marshy land namely Pallikaranai. It expands nearly 10 km north to south with around 3 km of width from west to east which is finally joints the Bay of Bengal through the Buckingham canal and Kovalam estuary. The collection and digestion of the surface water and Leachate samples were performed by following (Nollet, 2007). Water and Leachate samples amounting to 1 liters each were collected using polythene bottles. To avoid contamination, the polyethylene bottles were rinsed with 2% nitric acid prior collection of samples. They were stored in dark and refrigerated condition and were subjected to nitric acid digestion (Modified AOAC Official Method 974.27, 990.08 (1993).

## ACID DIGESTION AND HEAVY METAL ANALYSIS

In brief, 40 ml of the stored Water and Leachate samples was taken in a round bottomed flask and 5 ml of concentrated Nitric acid ($HNO_3$) was added followed by 2ml of concentrated Hydrochloric acid (HCl). The sample is evaporated and refluxed using condenser for 30 minutes. The process is continued for another 10 minutes after adding 5 ml of concentrated $HNO_3$ and 2ml of Hydrogen peroxide ($H_2O_2$). The the sample was allowed to cool and transferred to volumetric flask of 50 ml capacity. The sample is then made upto 50 ml by adding 2% $HNO_3$.

The floating vegetation namely, *Eichhorniacrassipes* was collected in polythene bags from 4 different sites in and around Pallikaranai marsh land. The samples were weighed fresh first and it was shade dried for 4 days. Post which, dry weight is measured and plants were cut into fragments for grinding. Thus ground samples were sieved to get fine particles and then were weighed. Later, 1gm of each sample was subjected to nitric acid digestion (Modified CIBA protocol, 2004). In brief 1 gm of dry powdered plant material was taken in a 250 ml RB flask and 5 ml of conc. $HNO_3$ followed by 2 ml of conc.HCl were added. It was left overnight undisturbed for 16 hrs. The contents were subjected to reflux condensing at 60 C. After 2 hrs 2 ml of $H_2O_2$ was added through the condenser and refluxed for 10 more minutes. The condenser was rinsed with 2% $HNO_3$ and was filtered using Whatman No.41 filter paper. Quantitatively the contents of the digest was made upto 50 ml using 2% $HNO_3$.

All the digest samples were analyzed for four heavy metals namely Cr, Cu, Cd and Pb using Flame Atomic Absorption Spectrophotometer (ELICO SL 243Double Beam AAS). The instrument setting and operational conditions were done in accordance with the manufacturer's specifications. CIBA

## THE DIFFERENT SAMPLES, SAMPLING SITES AND THEIR GPS COORDINATES

## STANDARD SOLUTION PREPARATION

3 standard calibration solutions that span the working ranges of the respective elements were prepared from 1000 ppm using 50ml standard volumetric flask for all the samples.

Preparation of Standard solution = Molecular weight / Atomic weight

## Transportation index (Ti)

The transportation index (Ti) provides the heavy metal concentration accumulated in root/leaf and represents the capacity of the plant to translocate specific metals from roots to leaves at varied concentrations (Ghosh, 2005)

Ti = Heavy metal in leaves $(mg/kg)^{-1}$/ Heavy metal in roots $(mg/kg)^{-1}$ * 100

Ti< 1 – low transportation index (Ti)

## RESULTS AND DISCUSSION

Fig. 3.Leachate and surface water and Floating Vegetation samples

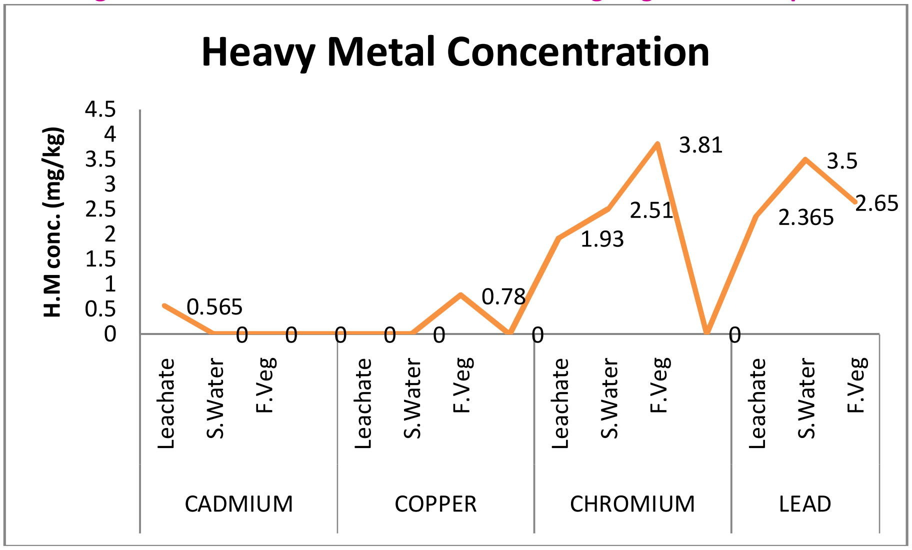



Table 2.

| SAMPLE | LEACHATE | | | | SURFACE WATER | | | | VEGETATION | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cd | Cu | Cr | Pb | Cd | Cu | Cr | Pb | Cd | Cu | Cr | Pb |
| **Mean** | 0.565 | 0 | 1.93 | 2.36 | BDL | BDL | 2.51 | 3.5 | 0 | 0.78 | 3.81 | 2.65 |
| **STDV** | 0.5 | 0 | 3.34 | 1.25 | NA | NA | 5.03 | 0.98 | NA | 0.37 | 4.02 | 1.27 |
| **Range** | 0.00-1.06 | 0 | 0.00-6.91 | 1.16-3.6 | NA | NA | 0.00-10.07 | 2.65-4.83 | NA | 0.66-1.39 | 1.47-9.93 | 0.72-3.31 |

*BDL – Below Detectable Level, NA – Not applicable

### Heavy Metal Concentration in Leachate

The concentration of heavy metals Cd, Cu, Cr and Pb were analyzed in four locations of Perungudi dump yard. The order of the heavy metal concentration was found to be Cu<Cd < Cr <Pb from lowest concentration to highest concentration. While copper was found to be below the detectable limit, the Cadmium concentration was estimated to be above the detectable limit ranging from 0.00 – 1.06 mg/kg with the average of 0.56 mg/kg. The concentration of Chromium was ranging from BDL- 6.91 with the average of 1.93 mg/kg. The average chromium content in the leachate sample is found to be above the permissible limit of BIS/WHO posing threat to ecosystem of the marsh land. Of all the four heavy metals Lead was estimated to be highest ranging from 1.16-3.6 with the average of 2.36 mg/kg which is above the permissible limit.

### Heavy Metal Concentration in Surface water

The concentration of copper and Cadmium in the surface water samples is found to be below the detectable level showing no significant contamination in the surface water body. The surface waters analysis done by Karpagavalli et al. (2012) in pallikaranai wetland was also found to be showing the least concentration level of Copper. The average concentration of Chromium in the surface water is found to be

2.41 mg/l wherein site 1 seems to be showing the highest concentration level of 10.07 mg/l while the rest of it are showing no significant presence of chromium. The lead content in all the four samples around pallikaranai was found to be showing the average of 3.5 mg/l ranging from 2.65 mg/L to 4.83 mg/L which is above the standard limit. Suggested by WHO, USEPA and BIS.

### Floating Vegetation

In both root and leaf samples of ***Eichhorniacrassipes***cadmium is found to be below the detectable limit while copper is recorded to be present but below the permissible limits of both BIS and WHO. While comparing the root and leaf samples of copper, root is found to be ranging from 1.31 – 2.69 with the average of 1.765 which is higher than the leaf which ranges from 0.00-0.9 with the average of 0.295 mg/kg. The concentration of Chromium in the vegetation is found to be ranging from 1.47-9.93 mg/kg with the average concentration of 3.81mg/kg. The vegetation is found to be loaded with an high concentration of lead than the rest of the heavy metals (Cd, Cu, Cr), which ranges from 0.72-3.31 with the average of 2.63 mg/kg which is above the permissible limits 2.5 mg/kg (BIS) and 0.3 mg/kg (WHO) mg/kg (**Adeola Alex Adesuyi, 2015**).

**Table 3. The mean concentration of heavy metals in Leachate, surface water (Mg/L) and in Floating Vegetation (mg/kg) and their permissible limits and their permissible limits (WHO/FAO and BIS)**

| SAMPLE | Cd | BIS | WHO /FAO (mg/ kg) | Cu | BIS | WHO /FAO (mg/kg) | Cr | BIS | WHO /FAO (mg/kg) | Pb | BIS | WHO /FAO (mg/kg) | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Leachate** | 0.56 | **0.003** | 0.01 | 0 | 0.05 | 1 | 1.93 | 0.05 | 0.05 | 2.36 | 0.01 | 0.1 | (WHO Drinking water standards. 1981)USEPA |
| Surface water | 0 | **0.003** | 0.01 | 0 | 0.05 | 1 | 2.51 | 0.05 | 0.05 | 3.5 | 0.01 | 0.1 | (WHO Drinking water standards. 1981)USEPA |
| **Floating veg** | 0 | 1.5 | 0.2 | 1.02 | 30 | 40 | 3.94 | NA | 2.3 | 2.63 | 2.5 | 0.3 | (Adeola Alex Adesuyi,et al. 2016) ThiliniKananke et al. (2014) |

## DISCUSSION

### Leachate

While the previous studies (vanitha*et al.* 2014, Kurien*et al*. 2003) show the below detectable level of Chromium in Perungudi Leachate, the present study indicates the increase of Cr in the sample. The enrichment of chromium is mainly due to the increased dumping of effluents of the chrome plating dyes in the dump yard and tanning of leathers from industries located in Chrompet near the study area. Invariably the concentration of the Lead is found to be above the permissible limit in all the four sites in Perungudi Leachate in contrast to the finding of Vanitha*et al.,* 2014 who detected the lower level of lead (0.09 ppm) in leachate samples of Perungudi. The concentration of copper is estimated to be 1.37 ppm in a study carried out by Vanitha*et al.* 2014 in Perungudi while the current study indicate reduction in the Cu content.

## SURFACE WATER

Higher concentrations of chromium was found in one of the four samples revealing Pallikaranai surface water contamination with Chromium as predicted by (Karpagavalli et al. 2012) in Pallikaranai whose study revealed that only Chromium was exceeding the prescribed limit in maximum sampling locations.Lead content in the surface water is estimated to be the highest of all the heavy metals with the average concentration of 3.5 mg/kg. The study carried out by (Jayanthi and Padmavati. 2014) has also revealed that the levels of Pb (average content of 0.06 mg/L) in the dug wells, tube wells and the surface water of Pallikaranai estimated to be above the desirable limit set by CPHEEO. The higher concentration of Lead (Pb) could be due to the Lead rich sources materials namely pyrotechniques, photography, petroleum, gasoline, paints, glassware, printing press and other wastes of the Chennai city that are dumped in the Perungudi dumping yard in a close proximity. Lead (Pb) is found to be in higher concentration in Pallikanai marsh land mainly due to anthropogenic intervention. It is also reported by (Abdel *et al.*1996) to be the major chemical pollutant of the environment there for, its concentration in vegetation in several countries has increased in recent decades owing to humankind's activities.

## Floating Vegetation

Water hyacinth (*Eichhorniacrassipes)* indicates the higher content of the pollutant in the Pallikaranaiwetland which is mainly due to the dump yard adjacent to it. The target plant's roots and leaves in the study has shown considerable bio-magnification as their roots naturally absorb pollutants 1000 times that of the surrounding water (Jafari*et al.* 2010).The distributive pattern of Cr, Cu, Zn and Pb were also found to be similar functioning as biomarkers of heavy metal contamination (Loska*et al.*2004). The dissemination of atmospheric and automobile exhaust could be causing rise in the concentration of Lead (Pb) in the locality of Pallikaranai as it is infested with automobiles around (Léopold *et al.* 2008). Besides Lead the highest accumulated heavy metal in this study pose grave threat as it gets deposited with age in bone aorta, kidney, liver and spleen. Food (65%), water (20%) and air (15%) are its major means of entry in to human body (RuqiaNazir*et al*. 2015).

## Transportation index (Ti)

The Hydrophytes in the aquatic system are found to be capable of absorbing heavy metals and widely extract high level of heavy metals through the roots and translocate them in the surface biomass (Ghosh, M 2005). The leaf/root heavy metal (Cu, Cr, Pb) transportation index (Ti) for the floating vegetation (*Eichhorniacrassipes*) is given in the figure 3. The order of the heavy metal Transportation was found to be Cd<Cu<Cr<Pb with 0, 0.64, 0.84, 1 respectively from lowest to the highest. *Eichhorniacrassipes*which is tested to be an indicator for the heavy metal (Abdel *et al.* 1996) is now found to be effectively transporting Pb and Cr to an extent. While the plant shows the almost higher transportation of Cr and Pb, it shows the considerable difference between root and leaf concentrations of Cu indicating an important block to get transferred from roots to the leaves. The ability of the plant to transportation Cd could not be estimated as its availability in the substrate itself was below the detectable level. The lower values of Ti/1, is most likely related to an exclusion strategy (Baker, 1981). Studies have affirmed (Ndeda, L. A. et al. 2014) that the floating vegetations display better metals translocation capacity than the emergent hydrophytes. The reason being wider surface area to free floating plants' wider surface area.

**Table 4. Transportation index (Ti) and Bio concentration Factor (BCF) of *Eichhorniacrassipes***

| H.Metals | CADMIUM | | COPPER | | CHROMIUM | | LEAD | |
|---|---|---|---|---|---|---|---|---|
| SAMPLES | Root | Leaf | Root | Leaf | Root | Leaf | Root | Leaf |
| SITE 1 | BDL | BDL | 1.73 | 0.9 | 0 | 3.33 | 3.05 | 3.52 |
| SITE 2 | BDL | BDL | 1.33 | 0 | 2.7 | 2.72 | 3.88 | 2.75 |
| SITE 3 | BDL | BDL | 2.69 | 0.1 | 0.7 | 2.24 | 3.25 | 3.18 |
| SITE 4 | BDL | BDL | 1.31 | 0.18 | 13.75 | 6.12 | 0.07 | 1.37 |
| SD | NA | NA | 0.64 | 0.41 | 6.41 | 1.73 | 1.69 | 0.94 |
| Mean | NA | NA | 1.76 | 0.29 | 4.28 | 3.6 | 2.56 | 2.7 |
| Range | NA | NA | 1.31-2.69 | 0.00-0.9 | 0.00-13.75 | 2.24-6.12 | 0.07-3.88 | 0.94-3.52 |

*BDL – Below Detectable Level, NA – Not applicable

**Figure-5**

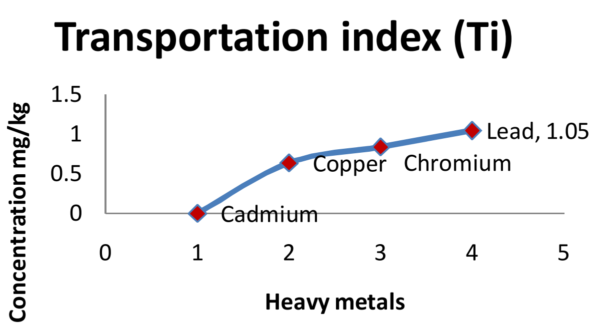
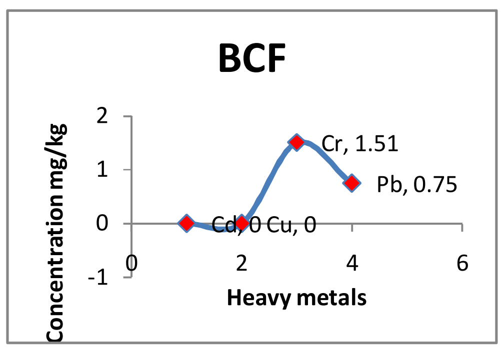



**Figure-6**




## Bio concentration Factor (BCF)

Bio-concentration factor is considered to be vital aspect in phytoremediation: the metals' absorption, their mobility through the plant tissue and their removal of the aerial plant biomass (McGrath, S.P.*et al*. 2003) The estimation of the heavy metals Bio concentration factor is carried out as follows (Zayed, A, 2014):

Bio concentration Factor (BCF) = the metal concentration of the plant tissue (mg/kg-1) / the metal concentration in external environment (mgL-1 or mg/kg-1)

The phytoaccumulation ability is indicated by the higher ratio of BCF

Heavy metals' order for the BCF values in floating vegetation*Eichhorniacrassipes*were as Cr >Pb> Cu>Cd in Pallikaranai wetland with 1.51 mg/kg, 0.75 mg/kg in Chromium and Lead respectively. The Study shows that the free floating vegetation *Eichhorniacrassipes* has recorded moderate Bio Concentration Factor and higher translocation Ability of heavy metals in the wetland polluted by heavy metals. (Ndeda, L. A. *et al*. 2014).

## CONCLUSION

The results obtained clearly shows that pallikaranai marsh land (lake) is highly polluted with Pb followed by Cr and Cu respectively due to the continuous discharge of different pollutants into it. It can also be concluded that the leaching of wastes from the Perungudi dump yard where the domestic and industrial wastes of Chennai Metro city are dumped could lead to the contamination of the Pallikarnai marsh land. Besides the southern drains namely leather factories around could play an important role in dissemination of chromium metal into the environment. The leaf/root transportation index (Ti) for the metals Pb, Cr and Cu in floating vegetation (*Eichhorniacrassipes*) is found to be highly promising. Thus the study indicates *Eichhorniacrassipes*, a floating vegetation is capable of phytoextraction anda potential plant for the process of phytoremediation. The work has revealed that *Eichhorniacrassipes* high bio concentration factor both in Cr as well as Pb. The Pallikaranai marsh land which is meant for improving water quality and faunal diversity has been badly damaged due to Perungudidump yard nearby, anthropogenic activities and other encroachments. Conscious and consistent efforts have to be taken by the corporation authorities to protect the marshland from further pollution by reducing and recycling the industrial and toxic effluents.

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