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Phytoextraction of Heavy Metals by Some Aquatic Macrophytes in Fresh Water Stretch of River Tapi at Surat City, Gujarat, India

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Abstract: ***The study was conducted to measure the concentrations of Cd, Co, Cu, Pb and Zn in fivedifferent species of aquatic macrophytes collected from fresh water stretch of Tapi river at Surat city of Gujarat. Plants along with surface sediments and water were analyzed for Cd, Co, Cu, Pb and Zn contamination. The plant species selected were: Eichornia cressipes (Mart.)Solms-Loub (root and shoot), Hydrilla verticillata (L.f.) Royle (whole plant), Persicaria glabra (Willd.)M.Gomez (root, stem and leaf), Pistia stratiotes L. (root and shoot) and Ceretophyllum demersum L. (whole plant). Samples were analyzed for heavy metals by AAS (Atomic Absorption Spectrophotometer). The greater accumulation of heavy metals was observed in the root of Pistia stratiotes. The lowest content was observed in the stem of Eichornia cressipes. Based on the concentration observed in the river's vegetation, the five heavy metals arranged in the descending order are: Zn > Cu > Pb > Co > Cd. The results of concentration of heavy metals in selected plants were compared with the standard, normal and critical toxicity range in plants. The detected value of Cd falls within normal range, while that of Co, Cu, Pb and Zn were within the critical range. However, Co and Cu showed the highest accumulation with alarming toxicity levels, which areconsidered as one of the most hazardous pollutants in river. Species like Hydrilla verticillata, Persicaria glabra and Pistia stratiotes are also proposed as phytoremediants, which are the most useful plant species in phytoremediation studies due to their ability to accumulate heavy metals in high concentration and their availability throughout the year.***

Keywords: Aquatic macrophytes, Phytoextraction, Tapi river, Heavy metals, Surat

1. Introduction

Heavy metal pollution is an important environmental problem in the world. In contrast with most organic materials, metals cannot be transformed by microorganisms and therefore accumulate in water, soil, bottom sediments and living organisms (Miretzky et al., 2004). Rapid urbanization, industrialization, excessive use of fertilizers and pesticides, etc. have resulted in heavy metal pollution of land and water resources. The increasing load of heavy metals has caused imbalance in aquatic ecosystems and the biota growing under such habitats accumulate high amounts of heavy metals (Cu, Zn, Cd, Cr, Ni, etc.) which in turn, are being assimilated and transferred within food chains by the process of magnification (Pergent &Pergent-Martini, 1999). Direct discharge or wet and dry depositions of contaminants increase the concentration of trace elements in aquatic systems, thus resulting in their accumulation in sediments (Dunbabin and Bowmer, 1992; Sinicropeetal., 1992).

Phytoremediation has several advantages and is the most significant one in study of sub-lethal levels of bioaccumulated contaminants within the tissues / components of organisms, which indicate the net amount of pollutants integrated over a period of time (Lovett-Doustetal., 1994). Macrophytes are considered as important component of the aquatic ecosystem not only as food source for aquatic invertebrates, but also act as an efficient accumulator of heavy metals (Janauer, 2001; Pajevićetal., 2001; Samecka-Cymerman &Kempers, 2002; Samecka-Cymermanetal., 2005).

Aquatic plants absorb elements through roots and / or shoots (Pip and Stepaniuk, 1992; Jackson, 1998). Various species show different behavior regarding their ability to accumulate elements in roots, stems and / or leaves. Therefore, it is useful to identify the plant organ that absorbs the greatest amount of trace elements (St-Cyr and Campbell, 1994; Baldantonietal., 2004). In aquatic systems, where pollutant inputs are discontinuous and pollutants are quickly diluted, analysis of plant components provides time-integrated information about the quality of the system (Baldantoni et al., 2005). Bioavailability and bioaccumulation of heavy metals in aquatic ecosystems is gaining tremendous significance globally. Several of the submerged, emergent and free-floating aquatic macrophytes are known to accumulate and bioconcentrate heavy metals producing an internal concentration several folds greater than their surroundings (Chen et al.,2008).

As the aquaticmacrophytes concentrate great amount of various substances (eg.Metals) and are consequently useful indicators of local pollution, the aim of present study was to assess the toxicity status induced by five heavy metals (Cd, Co, Cu, Pb and Zn) in fiveselected aquatic macrophyte species (passive biomonitors) in comparison with water and sediments.

2. Materials and Methods

2.1 Study area

Tapi River originates from Satpura Mountain in Betal district of Madhya Pradesh at an elevation of 725m above sea level. It has a drainage area of about 6400 km^2 and hourly flow of 120,000,000 cubic yards during the season of extended floods. It runs 724 km from its origin through three states (Madhya Pradesh, Maharashtra and Gujarat) before it joins the Arabian Sea (C.P.C.B., 1994). It has a dam over it at Ukai around 98 km away from the mouth of estuary and two Weirs, one at Kakrapar–70 km away from the mouth of estuary and another at Rander–15 km away from the mouth of estuary. There are many estuaries in Gujarat. Out of them Narmada and Tapi are larger ones. Tapi meets the sea near Surat city (21°12 N and 72°50 E). By the construction of Weir Cum Causeway at Rander in Surat in 1994, Tapi river has been divided into two, upstream of the Weir as a fresh water and downstream of the Weir as a marine inlet.

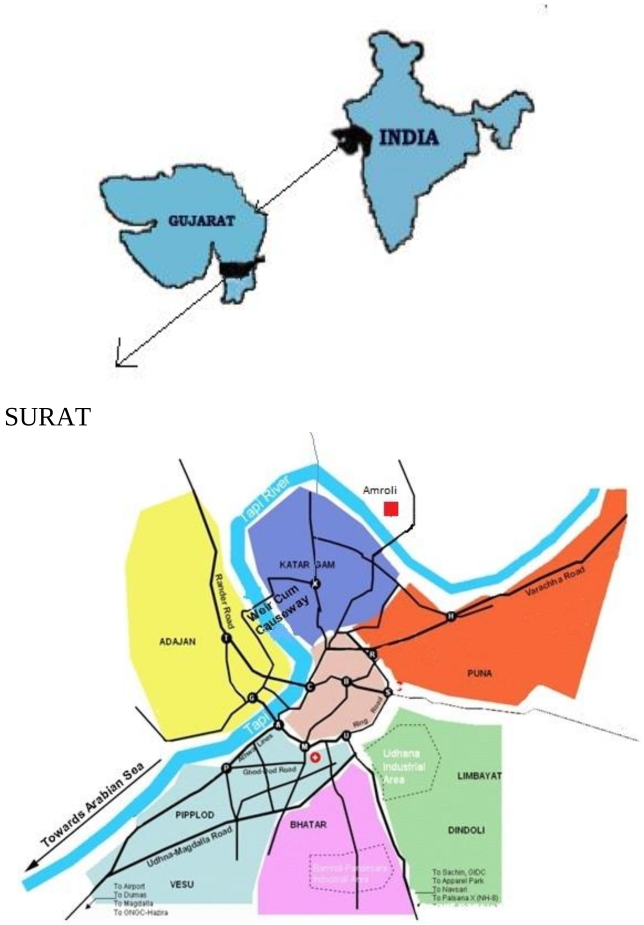

Figure 1: Map showing site location [W1 – Fresh water zone near Amroli (upstream of Weir Cum Causeway) and W2 - Estuarine region after Weir Cum Causeway (Downstream of Weir Cum Causeway)]

Surat is regarded as an industrial capital of Gujarat state. It has large number of chemical, diamond, textile, iron and steel, cement, pharmaceuticals and many other industries. As a result of rapidly expanding industrialization, urbanization and population blast, streams, lakes, ponds and other water bodies are being polluted. The untreated waste water thrown out by the industries in the river Tapi is the major cause of water pollution. The untreated waste water and sewage thrown in the river Tapi have also increased water pollution in this area. Due to lack of sanitation facilities polluted water enters directly into the river.Sediment, water and plant sample were collected from fresh water stretch near Amroli situated in upstream of weir cum causeway.

2.2 Water and sediment sampling

Surface water and composite sediment samples were collected at random from different areas of the river covering all directions. Soon after collection, the water samples were filtered through 0.45μm (poresize) Millipore filter and preserved in plastic bottles by the addition of a few drops of nitric acid. Sediment samples were preserved in air-dry plastic bags. The samples were labeled carefully and brought to the laboratory for further analysis.

2.3 Plant sampling

Five aquatic macrophytes from the river were selected as passive biomonitors for estimating the accumulation of five heavy metals (Cd, Co, Cu, Pb and Zn) by them. The plant species selected were : *Hydrilla verticillata* (L.f.) Royle (whole plant), *Eichornia cressipes* (Mart.)Solms-Loub (root and shoot),*Persicaria glabra* (Willd.)M.Gomez (root, stem and leaf) *Pistia stratiotes* L. (root and shoot) and *Ceretophyllum demersum* L. (whole plant). Healthy aquatic plants were collected, washed with river water to remove periphyton and sediment particles. Therefore, the element concentrations in the plant parts refer not only to tissue concentrations but also to adsorbed elements on plant surface. The collected plant species were placed in plastic bags, labeled carefully and brought to the laboratory. Polythene tools were used in sampling and storing the collected matrices to avoid the metal contamination. Plant species were identified according to Shah, 1978.

2.4 Chemical analysis of water, sediment and plant samples

Sediment samples were air-dried, sieved through 2mm governorates sieve and kept for analysis. Each fresh aquatic plant species sorted into different parts was dried at 80°C in hot air oven for 48hrs. The duplicate samples of water, sediment and plant-parts were chemically analyzed for detection of heavy metals (Cd, Co, Cu, Pb and Zn). Accurately 0.5g of dry powder of each sample was weighed, and digested with conc. HNO_3 and conc. H_3PO_4 (5:2) as prescribed by Jackson, 1960. Towards the end of the digestion, the flasks were brought to near dryness. The solutions were made to 100ml each in a volumetric flask with double distilled water. The water sample was prepared according to method of APHA 3030H (1975). The blanks were run with set, and the samples were analyzed in Atomic Absorption Spectrophotometer (AAS-4141, Electronic Corporation of India) at Navsari Agriculture University, Navsari, Gujarat. The concentrations of heavy metals such as Cd, Co, Cu, Pb and Zn were analyzed and calculated in mg/l for water and in mg/kg for sediment and plant samples. Mean values of duplicate subsamples of the water, sediment and plant samples were considered.

2.5 Data analysis

The values of the ratios between element concentrations in the sediments and those in the water were calculated. The mean values of heavy metals were calculated for water, soil and plant samples. Ranges of heavy metal contents and toxicity status in the tested plant species were compared with normal and critical ranges in plants. Correlation coefficient was calculated between metal-pairs in plants to check if differences exist between different metal combinations. The products of the correlation coefficient (r) were evaluated as follows:

1. 0–0.3: No correlation;
2. 0.3–0.5: Low correlation;
3. 0.5–0.7: Medium correlation;
4. 0.7–0.9: High correlation;
5. 0.9–1.0: Very high correlation

Mobility index was calculated for each level by using the formula:

$$\text{Mobility Index (MI)} = \frac{\text{concentration of metal in receiving level}}{\text{concentration of metal in source level}}$$

Mobility index showed bio mobility and transport of heavy metals through different levels, for example: water-root and root-shoot or water-root, root-stem and stem -leaf, which became functional to understand the transport mechanism of heavy metals in plant components such as root and shoot or root, stem and leaves.

3. Results

3.1 Water and sediments

The concentrations of the elements analyzed were far higher in the sediments than those analyzed in the river water filtered through Millipore filter (0.45µm opening size). Of the elements analyzed metal concentrations arranged in descending order for sediment sample are: Cu (160.8mg/kg) > Zn (137.8mg/kg) > Co (125.4mg/kg) > Pb (91.0mg/kg) > Cd (7.6mg/kg) and metal concentrations arranged in descending order for water sample are: Pb (0.314mg/l) > Co (0.266mg/l) > Cu (0.044mg/l) > Zn (0.018mg/l) > Cd (0.010mg/l). The values of the ratio between element concentrations in the sedimements and those in the water arranged in descending order are:

Table 1: Heavy metal concentration in sediments and water and ratios between the concentration in the sediments and that in the water

Element	Sediment (mg/kg)	Water (mg/l)	Sediment/Water
Cd	7.6	0.010	760.000
Co	125.4	0.266	471.429
Cu	160.8	0.044	3654.545
Pb	91.0	0.314	289.809
Zn	137.8	0.018	7655.556

Zn (7655.556) > Cu (3654.545) > Cd (760.000) > Co (471.429) > Pb (289.809) (Table 1).

3.2 Macrophytes

Table 2 shows the values of concentration of five heavy metals in analyzed plant parts of selected aquatic macrophytes along with mean values of heavy meal concentration in each selected plant part and mean concentration of each heavy metal in all selected plant parts.

Table 2: Heavy metal concentration in selected plant parts

ELEMENT/TAXON	Cd (mg/kg)	Co (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Total (mg/kg)	Mean (mg/kg)
C. demersum (whole plant)	6.2	58.2	78.0	94.2	83.6	320.2	64.04
E. cressipes (root)	4.4	49.8	67.6	38.4	78.6	238.8	47.76
E. cressipes (shoot)	5.4	14.8	79.8	50.2	18.8	169.0	33.80
H. verticillata (whole plant)	5.6	115.8	130.6	81.6	126.2	459.8	91.96
P. glabra (root)	7.0	48.2	212.6	128.4	131.4	527.6	105.52
P. glabra (stem)	5.4	34.0	170.2	62.8	82.2	354.6	70.92
P. glabra (leaf)	6.8	34.0	178.8	84.8	28.6	333.0	66.60
P. stratiotes (root)	6.2	91.8	322.6	113.0	340.2	873.8	174.76
P. stratiotes (shoot)	6.2	87.4	180.2	91.0	84.4	449.2	89.84
Total	53.2	534	1420.2	744.4	974.0		
Mean	5.91	59.33	157.82	82.71	108.22		

The mean concentration values of heavy metals in analyzed plant arranged in descending order are: Zn > Cu > Pb > Co > Cd. *P. stratiotes* (root) showed the highest capacity of accumulation with highest concentration of Zn(340.2mg/kg) and lowest concentration of Cd (6.2mg/kg) followed by *P. glabra* (root), *H. verticillata*(whole plant),*P. stratiotes* (shoot), *P. glabra* (stem),*P. glabra* (leaf),*C. demersum*(whole plant), *E. cressipes* root and *E. cressipes* (shoot)showed the lowest capacity of accumulation with highest concentration of Cu (79.4mg/kg) and lowest concentration of Cd (5.4mg/kg). In all the plants analyzed, more accumulation of heavy metals was observed in root system in comparison with that observed in shoot system.
The concentration of individual metal also varies from species to species. The content of Cd ranged from 4.4 mg/kg in *E. cressipes* (root) to 7.0 mg/kg in *P. glabra* (root). The Co content was found lowest in *E. cressipes* (shoot) (14.8 mg/kg) and highest in *H. verticillata* (whole plant) (115.8mg/kg). On the other hand, *E. cressipes* (root) showed lowest amount of Cu (67.6mg/kg), while highest amount of the same was recorded in *P. stratiotes* (root) (322.6mg/kg). Besides, lowest concentration of Pb was recorded in *E. cressipes* (root) (38.4mg/kg), while highest concentration of the same was observed in *P. glabra* (root) (128.4mg/kg). The minimum concentration of Zn was recorded in *E. cressipes* (shoot) (18.8mg/kg), while maximum content of the same was recorded in *P. stratiotes* (root) (340.2mg/kg).

Results of correlation coefficients calculated for different metal pairs showed that negative correlation was not observed in any metal pair. No correlation (0.0-0.3) was observed in a single metal pair, namely Cd and Zn. Law positive correlation (0.3–0.5) was observed in two metal pairs i.e., Co and Cu, and Co and Pb. Medium positive correlation (0.5-0.7) was observed in Cd and Cu, Co and Zn, and Pb and Zn. High positive correlation (0.7-0.9) was observed in four metal pairs, i.e., Cd and Co, Cd and Pb, Cu and Pb, and Cu and Zn.

Table 3: Correlation coefficient between concentrations of heavy metal-pairs in analyzed plant parts

Metal Pair	Correlation Coefficient
Cd × Co	0.721
Cd × Cu	0.554
Cd × Pb	0.869
Cd × Zn	0.174
Co × Cu	0.350
Co × Pb	0.393
Co × Zn	0.590
Cu × Pb	0.703
Cu × Zn	0.783
Pb × Zn	0.557

3.3 State of heavy metal pollution in plants

Comparing with standard normal and critical range in plants, the mean concentration of Cd (4.4-7.0 mg/kg) falls within the normal range whereas the mean concentrations of Co (14.8 – 115.8 mg/kg), Cu (67.6 – 322.6 mg/kg), Pb (38.4 – 128.4 mg/kg) and Zn (18.8 – 340.2 mg/kg) were recorded within critical range. Concentration of Co was encountered much higher than its critical range (1-8 mg/kg) in all plants analyzed, with the highest concentration in *H. verticillata* (whole plant) (115.8 mg/kg). Concentration of Cu was encountered higher than its critical range (25-90 mg/kg) in all plant parts analyzed except *C. demersum* (whole plant) and *E. cressipes* (root and shoot), but its concentration was far higher than its critical range in root of *P. stratiotes* (322.6 mg/kg). Thus Co and Cu seem to be hazardous in the study area, as their concentrations are extremely high.

Table 4: Ranges of heavy metals contents and toxicity status in the tested plant species, compared with normal and critical ranges in plants

Metal	Mean Range in tested plants (mg/kg)	Normal range in plants (mg/kg)*	Critical range in plants (mg/kg)*	Toxicity status
Cd	4.4-7.0	0.1-2.4	10-30	Normal
Co	14.8-115.8	0.75-1.07	1-8	Critical
Cu	67.6-322.6	7.53-8.44	25-90	Critical
Pb	38.4-128.4	0.2-20	30-300	Critical
Zn	18.8-340.2	1-100	100-400	Critical

** Data after Kabata-Pendias and Pendias (1992)*

3.4Transport of heavy metals through different levels

Mobility index (MI) showed biomobility and transport of heavy metals through different levels (Table 5). Present findings revealed that MI of Co (218.79) was lowest and that of Zn (4644.44) was highest in *C. demersum*, whereas in *H. verticillata* MI of Pb (259.87) was lowest and that of Zn (7011.11) was highest. Comparing other three plants, mean MI for water to root was found highest in *P. stratiotes* (5511.36),followed by *P. glabra* (2684.39) and *E. cressipes* (1330.06). In *P. stratiotes*,W-R MI of Zn (18900.00) was highest and that of Co (345.11) was lowest, whereas R-Sh MI of Cd (1.00) was highest and that of Zn (0.25) was lowest. In *E. cressipes*, W-R MI of Zn (4366.67) was highest and that of Pb (122.29) was lowest, whereas R-Sh MI of Pb (1.31) was highest and that of Zn (0.24) was lowest. In *P. glabra*, W-R MI of Zn (7300.00) was highest and that of Co (181.20) was lowest, whereas R-St MI of Cu (0.80) was highest and that of Pb (0.49) was lowest, whereas St-L MI of Cd (1.26) was highest and that of Zn (0.35) was lowest.

Table 5: Mobility indices of heavy metals through different organs of selected plants (W-P = Water to Plant, W-R = Water to Root, R-Sh = Root to Shoot, R-St = Root to Stem, St-L = Stem to Leaf)

Element	*C. demersum*	*H. verticillata*	*E. cressipes*		*P. stratiotes*		*P. glabra*		
	W-P	W-P	W-R	R-Sh	W-R	R-Sh	W-R	R-St	St-L
Cd	620.00	560.00	440.00	1.23	620.00	1.00	700.00	0.77	1.26
Co	218.79	435.34	184.96	0.30	345.11	0.95	181.20	0.71	1.00
Cu	1772.73	2968.18	1536.36	1.18	7331.82	0.57	4831.82	0.80	1.05
Pb	300.00	259.87	122.29	1.31	359.87	0.81	408.92	0.49	1.35
Zn	4644.44	7011.11	4366.67	0.24	18900.00	0.25	7300.00	0.63	0.35
Mean	1511.19	2246.90	1330.06	0.85	5511.36	0.72	2684.39	0.68	1.00

4. Discussion

The present study revealed that some of the aquatic plants possess greater accumulation ability for selected heavy metals. The aquatic plants growing in the study area exhibit different trace element concentrations. These results agree with the reports of Peverly (1985); Sawidis et al. (1995) and Abouel-kheir et al. (2007, a & b). In present study very high accumulation of Cu was found in root system (322.6 mg/kg) and in shoot system (180.2 mg/kg) of *P. stratiotes*, which indicates that *P. stratiotes* can be effectively used as phytoremediant for Cu contaminated water bodies. Cu was also found in very good amount in root (212.6 mg/kg), stem (170.2 mg/kg) and leaf (178.8 mg/kg) of *P. glabra*. Same way Cd, which is considered as one of the most toxic elements, was found in very higher amount in root (7.0 mg/kg) and leaf (6.8 mg/kg) of *P. glabra*, which suggests that *P. glabra* can remediate Cd contaminated sites more effectively. Concentration of Pb was found very high in *P. glabra* (root-128.4mg/kg and leaf-84.8 mg/kg), which indicates high potential of *P.glabra* to be used as phytoremediant at the sites contaminated by Pb, one of the most hazardous pollutants. *P. stratiotes* (root – 113.0 mg/kg and shoot – 91.0 mg/kg) also showed good capacity of accumulating Pb. High accumulation of Zn was found in root (340.2 mg/kg) of *P. stratiotes* and in root (131.4 mg/kg) of *P. glabra*, which suggest high potential of both these plants to remediate waters contaminated with Zn. *H. verticillata* also showed very good capacity of accumulating Zn with 126.2 mg/kg concentration.

Lovett-Doust *et al*. (1994) reported that the accumulation levels of pollutants in aquatic ecosystems may be higher in sediments than in plants. The present study agrees with this finding. Mean concentration of all elements in all selected plant parts were less in studied plants compared to the concentrations of the same elements in sediment.

The aquatic plants in the present study exhibited different heavy metal concentrations, depending on the plant organ. Roots of aquatic plants absorb heavy metals from the sediments and accumulate high concentrations (Baldantoni *et al*. 2004). Similarly our findings reveal the higher concentrations of all the studied heavy metals recorded in roots in comparison with shoots.

In all plants analyzed, mean concentration of metals were higher in root system compared to that in shoot system of the same plant. In *P. stratiotes* mean concentration of all metals in root was 174.76 mg/kg whereas that in the shoot system was 89.84 mg/kg. In *E.cressipes* mean concentration of all metals in root was 47.76 mg/kg whereas that in the shoot system was 33.80 mg/kg. In *P.glabra* mean concentration of all metals in root of was 105.52 mg/kg whereas that in the stem was 70.92 mg/kg and that in the leaf was 66.60 mg/kg. The probable reason for this is higher concentration of nutrients like sulphate, nitrate, nitrite, ammonia, phosphorus and organic matter as COD in river water in upstream compared to that in downstream. Due to higher concentration of nutrients in river water of upstream in comparison with that in downstream, probably the plants are absorbing less water in their aerial parts to fulfill the nutrient requirement and along with that less amount of water they are taking less heavy metals, which are dissolved in water, whereas situation at downstream is completely vice versa.

Comparing with permissible limits of heavy metals in water, the concentration of Pb and in river water was beyond the permissible limits of BIS (Bureau of Indian Standards), 2003. The concentration of Pb (0.314 mg/l) was at most alarming level which was six times more than the permissible limit (0.05 mg/l), which makes water toxic. Though the concentration of Co, Cu and Zn in river water were within the permissible limits as prescribed by BIS, 2003, due to its higher accumulation by aquatic plants, its concentration within the studied plants is in critical range. By the process of biomagnification, this critical concentration can enter the food chain and organisms can become victim of toxic effects of these heavy metals. So that it is not wrong to conclude that the permissible limits in water are not safe always.

Compared to the standard, normal and critical toxicity range of metals (Kabata-Pendias and Pendias, 1992) in selected plants, the accumulation of Cd was observed within normal range, while that of Co, Cu, Pb and Zn were registered within the critical range. However, Co and Cu showed the greater accumulation with alarming toxicity levels, which is considered to be the hazardous pollutants in river water.

5. Conclusion

It can be concluded from the present study that *H. verticillata*,*P. stratiotes* and *P. glabra* accumulated heavy metals in much higher concentration. Perhaps it might be the reason that these three species are more efficient in uptakeof heavy metals. Therefore these plants can be used more effectively as 'Phytoremediants' than other aquatic macrophytes.

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