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Evaluation of metal contamination and phytoremediation potential of aquatic macrophytes of East Kolkata Wetlands, India

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Objectives The present study analyzes metal contamination in sediment of the East Kolkata Wetlands, a Ramsar site, which is receiving a huge amount of domestic and industrial wastewater from surrounding areas. The subsequent uptake and accumulation of metals in different macrophytes are also examined in regard to their phytoremediation potential.

Methods Metals like cadmium (Cd), copper (Cu), manganese (Mn), and lead (Pb) were estimated in sediment, water and different parts of the macrophytes *Colocasia esculenta* and *Scirpus articulatus*.

Results The concentration of metals in sediment were, from highest to lowest, Mn (205.0±65.5 mg/kg)>Cu (29.9±10.2 mg/kg)>Pb (22.7±10.3 mg/kg)>Cd (3.7±2.2 mg/kg). The phytoaccumulation tendency of these metals showed similar trends in both native aquatic macrophyte species. The rate of accumulation of metals in roots was higher than in shoots. There were strong positive correlations ($p<0.001$) between soil organic carbon (OC) percentage and Mn (r=0.771), and sediment OC percentage and Pb (r=0.832). Cation exchange capacity (CEC) also showed a positive correlation ($p<0.001$) with Cu (r=0.721), Mn (r=0.713), and Pb (r=0.788), while correlations between sediment OC percentage and Cu (r=0.628), sediment OC percentage and Cd (r=0.559), and CEC and Cd (r=0.625) were significant at the $p<0.05$ level.

Conclusions Bioaccumulation factor and translocation factors of these two plants revealed that *S. articulatus* was comparatively more efficient for phytoremediation, whereas phytostabilization potential was higher in *C. esculenta*.

Keywords: East Kolkata Wetlands, Metals, Phytoremediation, *Colocasia esculenta, Scirpus articulatus*

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Introduction

Metal pollution has become a serious environmental threat since the Industrial Revolution. Wastewater from fertilizer, pesticide, cement, electroplating, painting, ceramics, battery, plastic, mining, and smelting industries are the major sources of metal contamination in aquatic environments. Domestic and municipal wastewater also contribute large amounts of different metals to the surrounding aquatic environment [1-4]. Essential metals such as iron, copper (Cu), manganese (Mn) and zinc (Zn) play an important role in biological systems, whereas some non-essential metals like cadmium (Cd), lead (Pb) and mercury are considered toxic even at low concentrations [5]. Essential metals also become toxic when they are present in higher concentrations for a longer period of time [6,7].

Wetlands, the common receivers of wastewater both from industrial and domestic areas, act as a natural filter, sink and transformation system for pollutants [8]. They perform numerous valuable functions like nutrient recycling and carbon sequestration, and they harbor large biodiversity [9]. However, for the last few decades, the deleterious impacts on wetland ecosystems due to anthropogenic activities have been increasing. East Kolkata (previously Calcutta) Wetlands (EKW), an important Ramsar site, is receiving a huge amount of industrial and municipal discharge from Kolkata Metropolitan area every day.

Phytoremediation is a natural, cost-effective and eco-friendly process in which plants reduce the contamination of a site [10,11]. In the case of metal pollution, some plants can remove the toxic metals from soil, sediments or water by accumulating them in their harvestable part (above ground biomass), whereas other plants can immobilize metals in soil or sediment by forming a zone surrounding their roots, preventing the metals from leaching into groundwater [12,13]. There have been reports on metal concentrations in water [14,15], soil [3,14,16], plants [3,14] and animals [14,17-20], but research into phytoremediation by native plants in this wetland (EKW) is scarce. The present study examines the concentration of Cd, Cu, Mn, and Pb in sediment of the EKW, and the possible phytoremediation of these metals by two native aquatic macrophyte species, *Colocasia esculenta* and *Scirpus articulatus*, based on two indices: transfer factor (TF) and bioaccumulation factor (BCF).

Materials and Methods

Description of Study Site

The EKW is situated in the eastern part of Kolkata city, India. They occupy a total area of about 125 km^2 and serve as a 'Natural Kidney' for Kolkata, whereby they are used to treat the huge amount of wastewater runoff from the city as well as nearby industries. This area's economy relies on agriculture and sewage-fed fisheries, and there are about 286 wastewater settling tanks used for fish culture [21]. Two native, aquatic, rooted macrophyte species (*C. esculenta* and *S. articulatus*) are dominant in this area and were selected for this study in order to investigate their bioaccumulation and phytoremediation potential.

Sample Preparation and Analysis

Thirteen different locations in the experimental site, the EKW was chosen (Figure 1). Samples of water, sediment and plants were collected in triplicate following the standard procedure of the American Public Health Association (APHA) [22]. Water samples were collected in acid treated polyvinyl containers and transported on ice-box to the laboratory, then stored at 4°C until analysis. A grab sampling method was used for collecting the water samples in plastic containers, which were rinsed with sample water three times. Water pH and electrical conductivity (EC) of the samples were measured using a multi-parameter tester (PCSTestr 35, Eutech Instruments, Singapore) in the field. For the metal analysis, 1 L of the water sample was acid-digested with nitric acid (HNO_3)-perchloric acid ($HClO_4$) following the standard procedure of APHA [22].

Sediment samples were collected from a depth of 0-20 cm. Surface and layered samples were collected randomly in two batches and then mixed for each site, before packing them in polythene bags. After reaching the laboratory, sediment samples were air-dried at room temperature and then sieved using a 2 mm mesh sieve. Sediment pH and conductivity were analyzed by sediment-water suspension (1:10 w/v ratio) with double distilled water from diluted (1:10 w/v ratio) air-dried sediment. Organic carbon (OC) percentage and cation exchange capacity (CEC) of sediment samples were analyzed following the methods adopted by Walkley and Black [23] and van Reeuwijk [24], respectively.

Plant samples were gently washed with deionized water, their root and shoot parts were separated, and they were dried at a

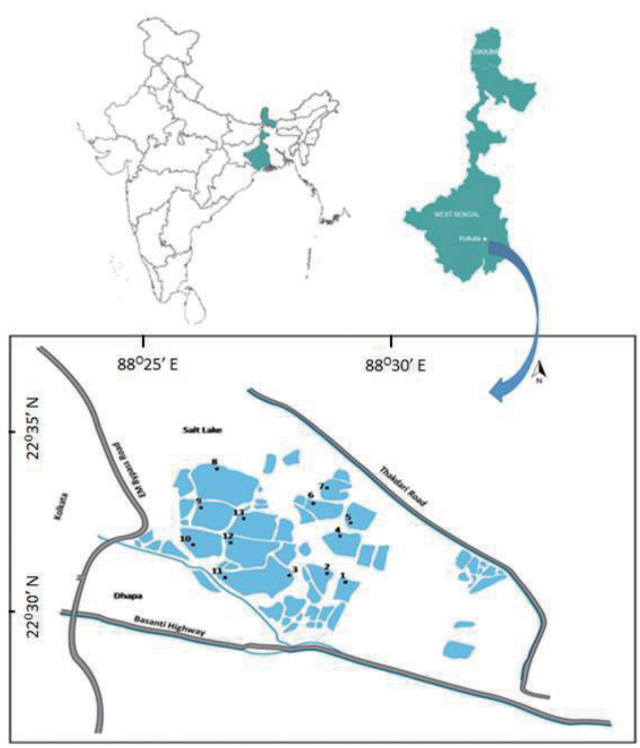

Figure 1. Location of the sampling sites.

constant 60°C in a hot air oven for 24 hours. For the metal analysis, sediment samples were digested with HNO_3-$HClO_4$ following the procedure described by Chen and Ma [25], and plant samples were digested with aqua regia–hydrogen peroxide as per the method of Mondal et al. [26]. Metals were analyzed using an atomic absorption spectrometer (GBC Avanta, Dandenong, Victoria, Australia).

Statistical Analysis

Statistical analysis was performed using the SPSS version 16.0 (SPSS Inc., Chicago, IL, USA). The correlation significance level ($p < 0.01$ and $p < 0.05$) between different sediment parameters and the concentration of metals is reported based on Pearson's correlation coefficients. Results are presented as the mean (± standard deviation) (n = 6).

Results

The concentrations of metals in water at 13 locations are presented in Table 1. The concentration of Cd ranged between 0.02 and 0.19 mg/L, Cu was between 0.02 and 0.03 mg/L, Mn varied between 0.12 and 3.23 mg/L, and Pb was found in the range of 0.10-0.92 mg/L. These results showed that the average concentrations of these metals in the water were in the order: Mn (1.67 ± 1.23) > Pb (0.28 ± 0.26) > Cu (0.09 ± 0.05) > Cd (0.02 ± 0.01).

Physicochemical characteristics of sediment are recorded in Table 2. Sediment pH varied from 6.97 to 7.46 with an average of 7.21 (± 0.32) indicating slightly alkaline nature. EC ranged between 193 and 578 μS/cm with an average of 338 (± 124) μS/cm. OC percentage and CEC were recorded between 0.95 and 3.66% and 0.26 and 1.91 meq of Na/100 g of soil, respectively. The average percentage of OC in the sediment was high (2.40 ± 1.17%). The average CEC was 1.14 (± 0.52) meq of Na/100 g of soil.

The concentrations of metals in sediment samples are given in Table 3. Cd concentration in the sediment ranged between 1.59 and 8.11 mg/kg, Cu between 19.4 and 48.5 mg/kg, Mn between 43 and 280 mg/kg, and Pb was recorded between 10.8 and 32.6 mg/kg.

The correlations between different sediment parameters and metals are given in Table 4. The pH and EC did not show significant correlations with other parameters. The OC percentage showed a strongly significant correlation ($p < 0.001$) with CEC (r = 0.819), Mn (r = 0.771), and Pb (r = 0.832). CEC also showed strong positive correlations with Cu (r = 0.721), Mn (r = 0.713), and Pb (r = 0.788). In addition, correlations between OC percentage and Cu (r = 0.628), OC percentage and Cd (r = 0.559), and CEC and Cd (r = 0.625) were significant at the $p < 0.05$ level.

The concentrations of Cu, Cd, Mn, and Pb in plant roots and shoots are given in Table 5. In *C. esculenta*, the average Cd, Cu, Mn, and Pb concentrations were 3.72 (± 1.90), 25.3 (± 15.0), 409 (± 210) and 22.8 (± 10.2) mg/kg dry weight (DW) in shoot, respectively; and 4.16 (± 1.98), 28.6 (± 8.77), 495 (± 119) and 25.5 (± 11.6) mg/kg DW in root, respectively. In *S. articulatus*, average Cd, Cu, Mn and Pb concentrations were 5.95 (± 3.07), 56.0 (± 16.5), 410 (± 111) and 26.2 (± 13.7) mg/kg DW in shoot, respectively; and 7.00 (± 1.66), 68.6 (± 22.7), 840 (± 349) and 27.3 (± 14.8) mg/kg DW in root, respectively.

Table 1. Concentrations of metals in water samples collected from the East Kolkata Wetlands

Sampling site	Cd	Cu	Mn	Pb
1	0.10±0.04	0.03±0.00	3.23±0.92	0.45±0.13
2	0.19±0.07	0.02±0.02	2.79±0.77	0.28±0.04
3	0.09±0.05	0.02±0.02	2.16±1.08	0.16±0.03
4	0.09±0.03	0.02±0.01	1.82±0.73	0.19±0.01
5	0.10±0.02	0.02±0.02	1.49±0.48	0.10±0.02
6	0.06±0.05	0.02±0.01	0.53±0.07	0.09±0.01
7	0.02±0.01	0.02±0.00	0.21±0.11	0.16±0.02
8	0.09±0.02	0.02±0.01	0.12±0.03	0.10±0.02
9	0.04±0.01	0.02±0.01	1.14±0.33	0.19±0.07
10	0.04±0.02	0.02±0.01	0.16±0.02	0.11±0.02
11	0.10±0.04	0.02±0.02	2.84±1.05	0.71±0.15
12	0.13±0.02	0.02±0.01	2.81±0.93	0.14±0.01
13	0.11±0.06	0.02±0.01	2.40±1.09	0.92±0.15

Values are presented as mean±standard deviation.
Unit: mg/L.
Cd, cadmium; Cu, copper; Mn, Manganese; Pb, lead.

Table 2. Physicochemical properties of sediment samples collected from the East Kolkata Wetlands

Sampling site	pH	EC (μS/cm)	OC (%)	CEC (meq of Na/100 g of soil)
1	7.05±0.10	290±53	2.61±1.14	1.28±0.55
2	7.25±0.26	309±95	3.22±1.05	1.45±0.48
3	7.30±0.29	311±109	2.05±0.90	1.12±0.28
4	7.46±0.22	247±64	2.75±1.14	1.43±0.48
5	7.35±0.17	430±70	2.53±1.60	1.28±0.28
6	7.25±0.30	223±33	1.40±0.40	0.64±0.28
7	7.25±0.08	355±112	2.41±1.76	1.12±0.28
8	7.02±0.63	224±120	0.95±0.73	0.65±0.26
9	7.10±0.83	374±93	1.93±1.34	0.80±0.28
10	7.24±0.56	578±87	1.28±0.71	0.42±0.14
11	7.37±0.06	476±60	3.66±1.06	1.59±0.28
12	6.97±0.41	380±49	2.83±1.03	1.44±0.47
13	7.11±0.38	193±56	3.61±1.22	1.62±0.25

Values are presented as mean±standard deviation.
EC, electrical conductivity; OC, organic carbon; CEC, cation exchange capacity; Na, sodium.

BCF and TF of the two plants *C. esculenta* and *S. articulatusare* given in Table 6. This study showed that in *C. esculenta*, BCF for Cd, Cu, Mn and Pb was 1.10 (±0.65), 1.14 (±0.52), 2.01 (±0.84) and 1.04 (±0.47), respectively; and in *S. articulatus* was 1.40 (±0.88), 1.79 (±0.94), 2.49 (±1.04) and 1.35 (±1.18), respectively; TF for Cd, Cu, Mn, and Pb was 0.67 (±0.50), 0.69 (±0.28), 0.88 (±0.41) and 0.59 (±0.25), respectively in *C. esculenta*, and 1.03 (±0.50), 1.10 (±0.61), 1.14 (±0.65) and 0.78 (±0.28), respectively in *S. articulatus*.

Discussion

Metal uptake by plants depends on pH, organic matter and CEC of the sediment [12]. Cu and Mn are the essential elements for plant growth, whereas Cd and Pb are toxic metals to plants. According to Kabata-Pendias and Pendias [27], 60-125 mg/kg of Cu, 70-400 mg/kg of Zn, 100-400 mg/kg of Pb and 3-8 mg/kg of Cd, based on total fractions in the soil, would be considered toxic to plants. The Cd content in the EKW sediment exceeds these ranges, indicating that plants in these wetlands are under stress. Chattopadhyay et al. [14] estimated the metal concentration in sediment of the EKW and found that Cu, Mn, and Pb concentrations were in the range of 0.01-1.49 mg/kg, 0.61-2.25 mg/kg and 0.25-1.46 mg/kg, respectively. High concentrations of Cu (210.0±17.0 mg/kg), Mn (552.0±14.9 mg/kg) and Pb (166.0±15.3 mg/kg) were reported in the sediment of the EKW by Chatterjee et al. [3]. Tang et al. [28] reported five times lower Cd level, 2.5 times lower Pb level and almost 1.5 times lower Cu level in wetland sediment of eastern China compared to the present study. Hu et al. [29] also reported a lower Cd level but higher Pb level in sediment of Dongting Lake. Therefore, the present study revealed that the EKW is under ill effects of heavy metal pollution. Higher metal concentrations were observed in this study in comparison to previous studies in the area due to differences in sampling location, as previous studies collected the sediment from wastewater carrying bottom sediment. The average metal concentration in the present study was, in order from highest to lowest: Mn (205.0±65.5 mg/kg) > Cu (29.9±10.2 mg/kg) > Pb (22.7±10.3 mg/kg) > Cd (3.67±2.22 mg/kg). A similar trend in the gradient of metal concentrations was also reported in sediment from different locations within the same wetland [3]. Metal undergoes physical, chemical and biological changes after discharging into the aquatic environment and usually binds with the particulate matter, ultimately settling down in the sediment [30]. Higher metal concentration in sediment than in water observed in the present study was also explained by previous research [5,12,30].

Strong positive correlations between OC and the heavy metals indicated regulated movement of heavy metals in the wetland environment as OC acts as a major sink for heavy metals (i.e., Cd, chromium, Cu, nickel, Pb, and Zn) due to its strong complexing capacity for metallic contaminants [31], which can also be related to the strong, positive correlation between heavy metals and sediment CEC. Additionally, this indicates that heavy

Table 3. Metal concentrations on a dry weight basis of sediment samples collected from the East Kolkata Wetlands

Sampling site	Cd	Cu	Mn	Pb
1	3.94±1.33	36.5±16.4	251±2	26.0±12.8
2	7.71±1.82	38.7±15.5	246±28	32.2±10.2
3	3.31±1.89	28.5±4.8	220±39	16.7±8.1
4	2.93±1.34	30.3±12.1	236±69	27.9±11.4
5	2.84±0.48	31.7±3.5	217±2	21.2±11.6
6	2.20±0.42	23.9±6.1	198±2	12.3±6.0
7	1.74±0.23	28.7±6.9	189±43	21.5±10.9
8	2.15±0.49	20.7±3.5	43±17	10.8±1.4
9	1.59±0.05	19.4±2.7	173±25	19.4±10.6
10	2.59±0.34	23.9±9.0	135±21	15.5±6.7
11	3.79±1.33	48.5±14.1	280±53	33.3±12.2
12	4.83±0.42	26.9±4.7	227±37	25.2±8.8
13	8.11±2.10	31.1±1.4	250±35	32.6±10.7

Values are presented as mean±standard deviation.
Unit: mg/kg.
Cd, cadmium; Cu, copper; Mn, manganese; Pb, lead.

Table 4. Correlation matrix (Pearson's correlation coefficients) of sediment properties and metals

	pH	EC	OC	CEC	Cd	Cu	Mn	Pb
pH	1							
EC	0.199	1						
OC	0.182	-0.043	1					
CEC	0.124	-0.162	0.819**	1				
Cd	-0.084	-0.175	0.559*	0.625*	1			
Cu	0.283	0.103	0.628*	0.721**	0.401	1		
Mn	0.267	0.088	0.771**	0.713**	0.397	0.627*	1	
Pb	0.127	0.035	0.832**	0.788**	0.652*	0.669*	0.725**	1

EC, electrical conductivity; OC, organic carbon percentage; CEC, cation exchange capacity; Cd, cadmium; Cu, copper; Mn, manganese; Pb, lead.
*$p<0.05$, **$p<0.01$.

metals in the wetland are originating from internal sources such as the predominant rocks [32]. The higher correlation between heavy metals observed in the present study can be explained by the salinity of the wetland. The lack of significant correlations between heavy metals and sediment pH and EC might be due to the narrow range of pH in the samples. Metal mobility is hindered by the slightly alkaline pH [32] and the lower mobility would favor metal accumulation in the soil [33].

The concentrations of Cu, Cd, Mn, and Pb in plant roots and shoots showed that roots accumulate greater concentrations than shoots, indicating high plant availability of the substrate metals as well as their limited mobility once inside the plant. The results are also supported by the findings of Outridge and Noller [34]. Tolerant species try to restrict the transfer of metals during sediment–root and root–shoot transfer [12,35]. These results showed that in general, the accumulation of metals was higher in root than shoot, and also revealed that the capacity for metal accumulation in *S. articulatus* was higher than in *C. esculenta*. The Cd concentration in both plant species examined in this study was within the range found in contaminated plants i.e., 5-30 mg/kg; and it indicates that *S. articulatus* was more efficient accumulate or than *C. esculenta* [27]. Likewise, the Cd concentration was also above the toxic level i.e., 20 mg/kg, as indicated by Borkert et al. [36], and *S. articulatus* showed a higher value than *C. esculenta*, indicating that *S. articulatus* was more good accumulator. Pb concentration in the plant parts was lower than the phytotoxic value 27 mg/kg in the case of *C. esculenta*, but higher in *S. articulates* [37], again implying that *S. articulatus* is more competent in accumulating the metals. Alloway et al. [38] also reported that metal bioaccumulation in plants varies from species to species. Uptake of metals by plants from soil generally occurs either passively, through the mass flow of water into the roots, or by active transport through the plasma membrane of root epidermal cells [12]. The plant is able to accumulate greater amounts of metal than is present in the surrounding medium [39]. The order of metal accumulation in these two plants both in shoots and roots was Mn > Cu > Pb > Cd.

The BCF of a plant indicates it sability to accumulate metal from the sediment in its shoots, whereas the ability of a plant to translocate it from root to shoot is expressed by the TF. These two factors are used to estimate the phytoremediation potential of a plant species [12]. Both BCF and TF values were higher in *S. articulatus* than *C. esculenta*. Ma et al. [10] reported that if a plant has TF and BCF values greater than 1, then it is a good accumulator plant. Accordingly, in the present study, *S. articulatus* acts as a better accumulator than *C. esculenta* due to its higher TF and its BCF being greater than 1. Higher accumulation of heavy metals in plants indicates lower concentrations of metal, both in the water and the sediment of the wetland. Therefore, *S. articulatus* acts as a greater phytoremediator of heavy metals than *C. esculenta* due to its higher translocation ability. Ma et al. [10] also reported that TF and BCF were greater than 1 in fern species for arsenic. In addition, the order of BCF and TF in both of the two plants studied here was: Mn > Cu > Cd > Pb. Phytostabilization is a property of plants that reduces the mobility of metal ions in the sediment. Through this process, plants bind the metal in the root or help in precipitation within the rhizosphere. According to Miller [40], plants with greater root biomass have the ability to immobilize contaminants by holding them in their roots. As a result, the leaching of metal to groundwater can be prevented, and the contamination of the food chain by metals can also be reduced [12]. Yoon et al. [12] stated that plants with high BCF but low TF can also be used for phytostabilization. In this study, both plant species examined are

Table 5. Concentrations on a dry weight basis of cadmium (Cd), copper (Cu), manganese (Mn) and lead (Pb) in shoot and root of *Colocasi aesculenta* and *Scirpus articulatus*

Plant name	Cd		Cu		Mn		Pb	
	Shoot	Root	Shoot	Root	Shoot	Root	Shoot	Root
C. sculenta	3.72±1.90	4.16±1.98	25.3±15.0	28.6±8.8	409±210	495±119	22.8±10.2	25.5±11.6
S. articulatus	5.95±3.07	7.00±1.66	56.0±16.5	68.6±22.7	410±111	840±349	26.2±13.7	27.3±14.8

Values are presented as mean±standard deviation.
Unit: mg/kg.

Table 6. Bioaccumulation factor (BCF) and translocation factor (TF) of cadmium (Cd), copper (Cu), manganese (Mn) and lead (Pb) of *Colocasia esculenta* and *Scirpus articulatus*

Plant name	Cd		Cu		Mn		Pb	
	BCF	TF	BCF	TF	BCF	TF	BCF	TF
C. sculenta	1.10±0.65	0.67±0.50	1.14±0.52	0.69±0.28	2.01±0.84	0.88±0.41	1.04±0.47	0.59±0.25
S. articulatus	1.40±0.88	1.03±0.50	1.79±0.94	1.10±0.61	2.49±1.04	1.14±0.65	1.35±1.18	0.78±0.27

Values are presented as mean±standard deviation.

suitable for phytostabilization due to their comparatively high BCF and low TF values. In particular, here *C. esculenta* has more potential for phytostabilization than *S. articulatus* and this may be due to differences in their root structure system. This study suggests that these two plants could be utilized for natural attenuation of metals in contaminated soil.

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Conflict of interest

The authors have no conflicts of interest associated with material presented in this paper.

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