

# Monitoring waste metal pollution at Ganga Estuary via the East Calcutta Wetland areas

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**Abstract** East Calcutta Wetlands, a Ramsar site, receives a huge amount of the city's composite industrial effluent (~600 million liters per day) throughout the year. The waste-element-contaminated water flows down through a major storm water flow (SWF) canal into the wetland for nearly 40 km farther eastward and is finally discharged into Kultigong river that flows through the eastern limit of the wetland and that in turn unites with river Ganga. Elemental load in water and bottom sediment at selected sites of the SWF canal was assessed by proton-induced X-ray emission and atomic absorption spectroscopy techniques. Gradual decrease in concentration levels of elements was observed in both water and bottom sediments of SWF canal up to its site of confluence at Kultigong, indicating nat-

ural remediation processes taking place along the canal up to the confluence at Ganga estuary. Any further conversion of this wetland area should be prevented to get the benefit from this no-cost natural cleanup process in connection to pollution prevention.

**Keywords** Wetland · Heavy metals · Wastewater · Bottom sediment

## Introduction

Along the levee of river Ganga, the city of Kolkata (formerly, Calcutta) has grown. This densely populated city at eastern India (a density of 43,413 persons per square kilometer within urban city limit in 2001; source: [www.demographia.com](http://www.demographia.com)) is sustained by a typical water scheme, having a natural slope towards east and southeast. The river Ganga flows along the west of the city. About 40 km eastwards of the metropolis, another river is present, named river Kultigong, which eventually unites with river Ganga. Beyond the eastern edge of the city, a vast wetland area (around 12,500 ha), the East Calcutta Wetlands (ECW), is present. This wetland designated as a Ramsar site (Ramsar site no. 1208; Wetland International site reference no. 2IN013), among 25 such other sites present in India and 1847 wetlands in the world, is a wetland of international importance

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for its multiple uses. For conservation and wise use of natural resources of wetlands, the “Convention on Wetlands (Ramsar, Iran, 1971)” was adopted on 2 February 1971 in the Iranian city of Ramsar, which is an intergovernmental treaty and popularly known as “Ramsar Convention” (source: [www.ramsar.org](http://www.ramsar.org)). ECW is a perfect example of wise-use wetland ecosystem, having a combination of environmental protection and development management through resource recovery practices adopted by local farmers exercising agriculture and pisciculture using composite city sewage (source: [www.wfindia.org](http://www.wfindia.org)).

However, ECW receives a huge amount of the city’s composite untreated wastewater, which is about 600 million liters a day (Chattopadhyay et al. 2000). This wastewater after being carried into different pumping stations by underground sewers is being pumped into open canals traversing the wetland via nine important drainage pumping stations. Throughout the year, the composite effluents are carried by water from around 6,000 different industries like tanneries and several other small-scale establishments such as battery, electroplating, rubber, pottery, and pigment manufacturing units, as well as the city’s urban sewage. This huge amount of composite raw effluent flows via the storm water flow (SWF) canal for nearly 40 km farther eastward and is finally

discharged in the Kultigong river (Ghosh 2004; Chattopadhyay et al. 1999, 2004).

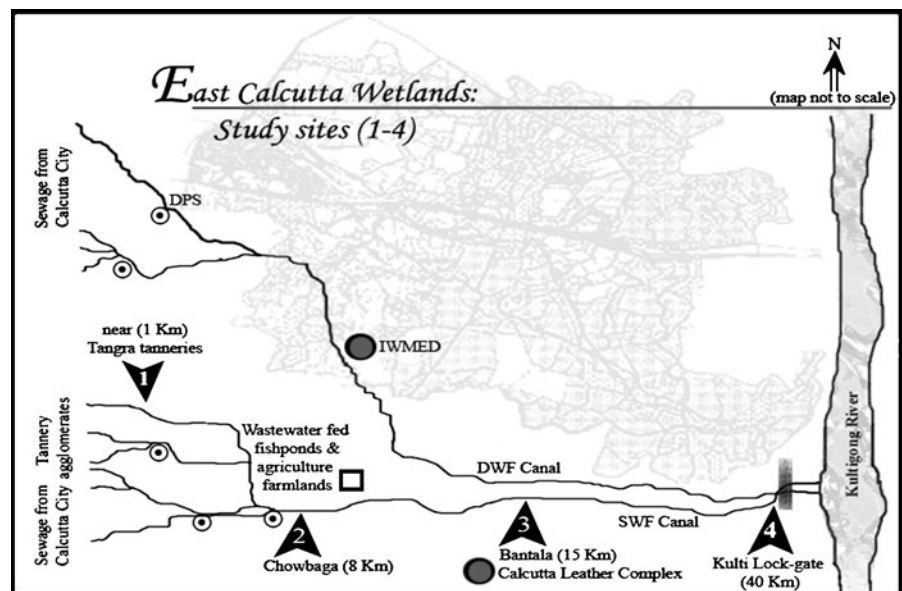
The first planning of the city drainage was made in 1803, though improved alternative arrangement of the present drainage scheme became functional in early 1890s. In the early 1930s, the SWF canal was excavated to drain the city’s ever-increasing amount of wastewater through wetland ecosystem to Kultigong river (Ghosh and Ghosh 2003). Concern of the potential impact of discharge and dumping of untreated industrial effluents tainted with different heavy metals had developed considerable momentum in today’s world in the perspective of sustainable development (Okoronkwo et al. 2005). This study was therefore initiated to monitor the concentration profile of different elements, viz., S, Ca, Cr, Mn, Fe, Ni, Cu Zn, Rb, Sr, and Pb, in water and sediments at selected spots of the SWF canal, which has significant importance as this water is finally being carried away into the river Ganga via Kultigong.

## Materials and methods

### Sampling sites and sample collection

Sampling was made at four selected sites along the major SWF canal (Fig. 1) passing through the

**Fig. 1** Selected study sites along the SWF canal in the East Calcutta wetlands



ECW (lat. 22° 27'–22° 40' N; long. 88° 27'–88° 35' E) area. Site 1 is located around 1 km away from Tangra tannery agglomerate (China town) of Kolkata on a canal carrying raw composite tannery effluent. Site 2 is located at Chowbaga, beyond 8 km from the source point, where the composite tannery effluent is siphoned into the SWF canal being mixed with municipal sewage. Site 3 is on the SWF canal near the projected Calcutta Leather Complex at Bantala, around 15 km away from the source point. Site 4 is on the same canal near Kultigong lock gate, around 40 km away from the source point. Samples (water and bottom sediment) were collected from the selected sites of the SWF canal throughout the year, during the first week of each month and three selected times of the day between January and December 2002. Water was collected in clean stopper glass bottles (1 L) by immersing them completely into the water (about 10–12 cm below the surface of the water to avoid floating debris; Nyangababo et al. 2005). Bottom sediments were collected from the upper 10-cm layer of the canal sites using Ekman dredge.

#### Analysis of samples

Detection of elements in the samples was done by proton-induced X-ray emission technique after preparation of targets. Thin targets (water) were prepared on 25-mm-diameter Nucleopore membranes with pore size of 0.4  $\mu\text{m}$  following the technique used by Aprilesi et al. (1984). Thick targets (bottom sediment) were prepared by making pellets of 10-mm diameter and mixing dry powdered samples and pure graphite (7:3). Blank targets, comprising the chemicals used and the National Institute of Standards and Technology (NIST) standard, were also prepared in the same way (water: standard reference material (SRM) 1643d; estuarine sediments 1646a). Targets were analyzed using 2-mm collimated 3-MeV proton beam, generated from a 3-MV tandem pelletron accelerator (at the Institute of Physics, Bhubaneswar, India). The characteristic X-rays produced from the samples were extracted through a 25- $\mu\text{m}$  Mylar window and detected by a Si(Li) detector (Canberra SL 30160 with active area of 30.2  $\text{mm}^2$ , Be window thickness of 8  $\mu\text{m}$  and resolution of 170 eV at

5.9-keV Mn X-ray) placed at 90° to the beam axis. Each sample was irradiated with and without a 25- $\mu\text{m}$  Al absorber. The beam current varied between 6.0 and 50.0 nA depending on the sample and use of absorber, maintaining a count rate of about 800 cps for each run, to avoid pileup. The data were analyzed by using GUPIX software as described in earlier reports (Chatterjee et al. 2007; Sudarshan et al. 2000).

Furthermore, samples were subjected to analysis by flame absorption mode of atomic absorption spectrophotometer (Perkin-Elmer AAnalyst-100 with interfacing AAWinlab Software), using element-specific hollow cathode lamps in default condition. Sensitivity and calibration of the instrument as recommended by Perkin-Elmer were also carried out (Chatterjee et al. 2006). For elemental analyses, acid extraction of samples was done following methods clarified elsewhere (Welz and Sperling 1999; Chatterjee et al. 2006). In brief, water samples were acidified with concentrated nitric acid to a pH less than 2.0 after filtration for analysis. Bottom sediments were dried, homogenized, and sieved for elemental extraction from dry ashes. About 1.0  $\pm$  0.05-g dried and grounded soil sample was ignited in a Muffle furnace at 500°C for 3 h. Acid extraction process from the ash produced in the furnace was done using concentrated HCl (Merck India) and concentrated HClO<sub>4</sub> (70% pure, Merck India). Reference materials (water: SRM 1643d, estuarine sediments 1646a) obtained from the NIST were also prepared in a similar method.

#### Studies on physicochemical parameters of wastewater

Physicochemical factors of wastewater of canal were also examined along with the samples collected each time. Potentiometric determination of pH, total dissolved solids (TDS), and dissolved oxygen (DO; using Multiline P4 (WTW, Germany) and Mettler Checkmate 90 (Toledo)), calorimetric and titrimetric determination of NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, total hardness, carbonate hardness, alkalinity, and acidity (using E. Merck, Germany, Field Testing Aquamerck reagent kits), and gravimetric analyses of total suspended solids (TSS) were done following standard methods (Eaton

et al. 1995). pH and other reagent factors were determined in the laboratory using a Mettler Autotitrator DL25.

### Statistical analysis

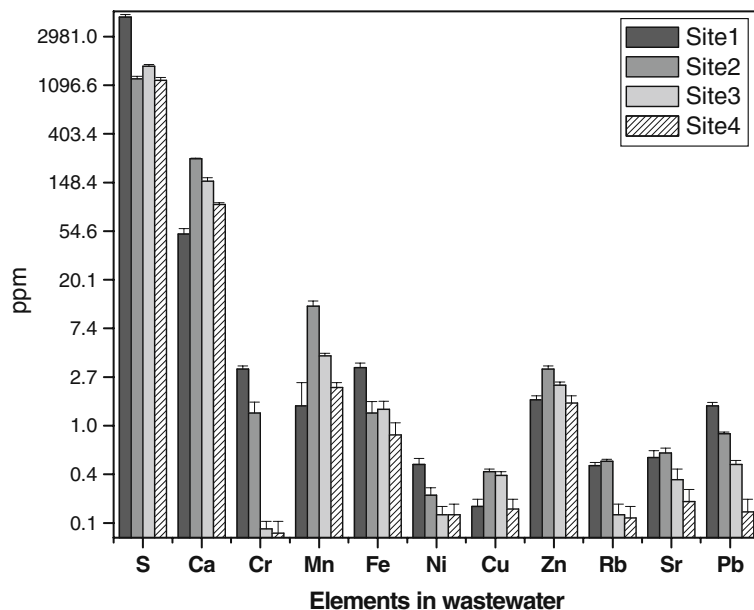
Analytical results were evaluated using SPSS (version 14.0). The standard deviation values were calculated, and the representative graphs were made using Origin (version 6.1). ANOVA (*F test*) was performed to compare the different sites studied. Other statistical analyses like principal component analysis and determination of correlation matrix and clusters were performed using SPSS (version 14.0) to evaluate further the different components and parameters of the dataset.

### Results and discussion

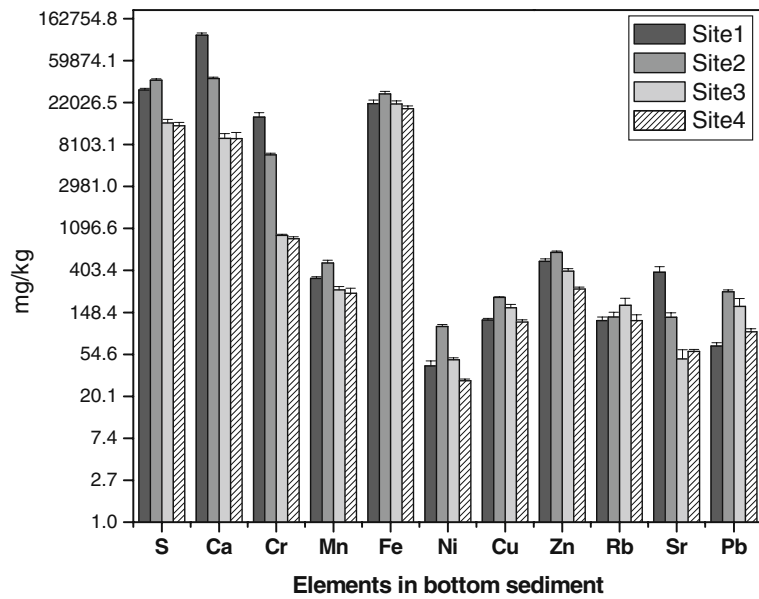
Variation of the concentration levels of different elements in SWF canal wastewater and bottom sediment of four selected sites (sites 1–4, designated as WW1–WW4 for water and BS1–BS4 for bottom sediment) was depicted in Figs. 2 and 3. Physicochemical factors of the wastewater of the SWF canal of the selected sites were depicted in

Table 1. The physical features of the same SWF canal and water flow rate at the selected sites were presented in Table 2, which showed gradual increase of the canal width and depth from site 1 to site 4. The average flow rate of the water along the canal in different sites was  $0.176 \text{ m s}^{-1}$  ( $0.061\text{--}0.333 \text{ m s}^{-1}$ ). In the present study, concentrations of S and Ca were recorded as highest among all other elements in water and bottom sediment, respectively. The highest concentrations of Ca and Mn were recorded in WW2 ( $241.2 \pm 3.27$  and  $11.7 \pm 1.25 \text{ mg L}^{-1}$ ) and the lowest in WW1 ( $51.5 \pm 6.01$  and  $1.5 \pm 0.92 \text{ mg L}^{-1}$ ). Cr, a major constituent of tannery effluent, was recorded highest in WW1 ( $3.2 \pm 0.21 \text{ mg L}^{-1}$ ). Fe and Ni concentrations were recorded highest in WW1 ( $3.3 \pm 0.33$  and  $0.45 \pm 0.06 \text{ mg L}^{-1}$ ). Interestingly, Cu and Zn concentrations were recorded highest in WW2 at  $0.39 \pm 0.03$  and  $3.2 \pm 0.21 \text{ mg L}^{-1}$ , respectively. Concentration of Pb was  $1.5 \pm 0.11 \text{ mg L}^{-1}$  in WW1; however, a gradual decline in the concentration level from WW2 ( $0.85 \pm 0.03 \text{ mg L}^{-1}$ ) to WW4 ( $0.17 \pm 0.05 \text{ mg L}^{-1}$ ) was evident from the study. The concentrations of Ca and Cr in BS1 were recorded highest ( $110, 078.9 \pm 5, 442.51$  and  $15, 561.1 \pm 1,824.11 \text{ mg kg}^{-1} \text{ dw}$ , respectively). While in BS2,

**Fig. 2** Elemental concentrations in the water of the SWF canal collected from selected study sites (sites1–4)



**Fig. 3** Elemental concentrations in bottom sediments of the SWF canal collected from selected study sites (sites 1–4)



concentrations of S ( $37,544.4 \pm 1,414.20 \text{ mg kg}^{-1} \text{ dw}$ ), Fe ( $27,110.8 \pm 1,696.91 \text{ mg kg}^{-1} \text{ dw}$ ), Mn ( $481.8 \pm 31.08 \text{ mg kg}^{-1} \text{ dw}$ ), Ni ( $105.9 \pm 5.22 \text{ mg kg}^{-1} \text{ dw}$ ), Cu ( $212.1 \pm 3.14 \text{ mg kg}^{-1}$ ), Zn ( $621.1 \pm 21.28 \text{ mg kg}^{-1} \text{ dw}$ ), and Pb ( $241.9 \pm 12.71 \text{ mg kg}^{-1} \text{ dw}$ ) were recorded highest in comparison with other sites.

It was apparent from the study that bottom sediment concentrations of all elements studied had a higher concentration level than that of overlying water. This was due to the constant sedimentation process occurring naturally throughout the year along the wastewater-carrying canal (DePinto and Martin 1980). Element-specific rate of sedimentation from the water into the bottom

sediment in canal was apparent in the study, indicating the role played by different factors including metal-metal interaction in this environment (Bryan and Langston 1992; Vallius 1999). In the present study, concentration of Pb was reduced by 43% from WW1 to WW2; however, in BS2, Pb was increased by 72% compared with that in BS1. Comparable interesting phenomenon can be found in case of some of major elements of the study site like S, Ca, Fe, and Ni. Mobility of different elements was very much related with organic matters, pH, salinity, and temperature of the aquatic environment (Liang 2007; Liang and Wong 2004). However, the higher concentrations of elements namely, Mn, Cu, Zn, and

**Table 1** Physicochemical factors of wastewater of the SWF canal of the selected sites (with  $\pm$ SD)

Parameters	Unit	Site 1	Site 2	Site 3	Site 4
Water temperature	$^{\circ}\text{C}$	$25.8 \pm 2.14$	$25.2 \pm 2.17$	$24.9 \pm 2.11$	$24.5 \pm 2.36$
pH		$7.7 \pm 0.52$	$7.5 \pm 0.54$	$7.2 \pm 0.65$	$7.6 \pm 0.76$
Dissolved oxygen	$\text{mg L}^{-1}$	$0.01 \pm 0.06$	$0.10 \pm 0.021$	$1.2 \pm 0.54$	$3.4 \pm 1.25$
$\text{Cl}^{-}$	$\text{mg L}^{-1}$	$3,659.2 \pm 441.82$	$1,631.2 \pm 134.54$	$715.5 \pm 83.30$	$510.2 \pm 71.32$
$\text{NO}_3^{-}$	$\text{mg L}^{-1}$	$40.5 \pm 22.30$	$42.1 \pm 35.12$	$33.5 \pm 22.69$	$62.0 \pm 21.80$
TSS	$\text{mg L}^{-1}$	$1,323.2 \pm 278.59$	$364.4 \pm 145.37$	$99.5 \pm 57.89$	$66.6 \pm 48.84$
TDS	$\text{mg L}^{-1}$	$5,658.1 \pm 454.76$	$2,376.1 \pm 534.87$	$967.6 \pm 257.35$	$766.0 \pm 133.90$
Alkalinity—M	$\text{mmol L}^{-1}$	$32.1 \pm 13.83$	$63.3 \pm 41.23$	$21.2 \pm 16.22$	$11.0 \pm 6.91$
Acidity—P	$\text{mmol L}^{-1}$	$1.2 \pm 0.62$	$0.72 \pm 0.42$	$0.7 \pm 0.32$	$0.6 \pm 0.33$
Total hardness	$\text{mg L}^{-1}$	$964.5 \pm 146.46$	$682.6 \pm 196.36$	$248.8 \pm 66.47$	$176.8 \pm 63.27$
Carbonate hardness	$\text{mg L}^{-1}$	$765.3 \pm 136.20$	$538.7 \pm 137.53$	$172.0 \pm 87.30$	$87.2 \pm 65.90$

**Table 2** Water velocity and canal characteristics in selected sites

	Unit	Site 1	Site 2	Site 3	Site 4
Water velocity*	m s <sup>-1</sup>	0.161	0.333	0.062	0.15
Width	M	1.67	25.17	45.34	82.68
Depth	M	0.45	1.01	1.71	2.7
Bed slope		1/5,084	1/15,676	1/25,356	1/20,674

\*Velocity of water at the surface level

Rb in wastewater and bottom sediment of site 2 were because it was the site of confluence and because of the fresh inputs of several elements from municipal sewage with the existing industrial wastewater-carrying canal. Concentration of Cr was recorded highest in the site 1, as in this site the wastewater-carrying canal was primarily shipping the wastewater from tanneries and other industries, conforming the anthropogenic sources for Cr pollution in the environment (Stoecker 2004). Principal component analysis (varimax with Kaiser normalization) was carried out for different variables of the contaminated site, and the range of factor loading (FL) between 0.25 and 1.0 for each component was accentuated. As per the highest factor loading for elements, the first component follows the sequence: Pb (FL = 0.989) > Ni (FL = 0.984) > Cr (FL = 0.983) > Fe (FL = 0.973) > S (FL = 0.932) and similarly, for second component, Mn (FL = 0.961) > Zn (FL = 0.894) was evident from the study. Interestingly, when physicochemical parameters were analyzed correspondingly as mentioned above, high factor loading was observed for component 1 in case of acidity (FL = 1.000) > Cl<sup>-</sup> (FL = 0.993) > TDS (FL = 0.991) > TSS (FL = 0.983), for component 2 in case of water velocity of the canal (FL = 0.932) > alkalinity (FL = 0.928) > water temperature (FL = 0.829), and for component 3 in case of pH (FL = 0.938). In addition, the correlation between elements and water parameters showed an interesting result. As for example, Cr speciation was highly correlated with TSS ( $r = 0.985$ ;  $p < 0.05$ ), TDS ( $r = 0.988$ ;  $p < 0.05$ ), total hardness ( $r = 0.965$ ;  $p < 0.05$ ), and carbonate hardness ( $r = 0.960$ ;  $p < 0.05$ ); likewise, S was highly correlated with water temperature ( $r = 0.988$ ;  $p < 0.05$ ); Ca with TSS ( $r = 0.996$ ;  $p < 0.05$ ), TDS ( $r = 0.999$ ;  $p < 0.05$ ), and Cl<sup>-</sup> ( $r = 0.998$ ;  $p < 0.05$ ); Mn with water temperature ( $r = 0.957$ ;  $p <$

0.05) and alkalinity ( $r = 0.990$ ;  $p < 0.05$ ); and Ni, Fe, and Zn with alkalinity ( $r = 0.960$ ,  $r = 0.988$ , and  $r = 0.952$ ;  $p < 0.05$ , respectively). Toxic metal Pb was correlated with water temperature ( $r = 0.764$ ;  $p < 0.05$ ), alkalinity ( $r = 0.788$ ;  $p < 0.05$ ). According to some earlier reports (Khagan et al. 1996; Mehta and Churi 1996), the removal of metal ions from solutions depends on pH between 3.0 and 6.5. However, in the present study, in the pH range of 7.2–7.7, no significant correlation was recorded between metal concentrations and pH values. On the other hand, metal concentrations showed significant positive correlation with water temperature, alkalinity, hardness, TSS, TDS, and chlorides. Most of the chemical processes like precipitation, nucleation, crystal growth, and biomineralization in aquatic systems occur at solid–water interface, regulating the composition of the wastewater and sediments (Stumm 1996; Bradl 2004). Quiescent flow of water along the canal (Table 2) enhanced settling process and caused less scouring and erosion, leading to gradual decrease of suspended particulates and increase of DO across the canal length. As the TSS load decreased along the course of the canal, light penetration increased; a good number of primary producers changed the oxygen environment of the wastewater, encouraging the secondary producers to step in (Chattopadhyay et al. 2000). Overall, increased productivity resulted in greater organic soil formation that enhanced the accretion necessary to offset the subsidence that could contribute to wetland loss. Besides, redox potentials of soil components also have a crucial impact on the behavior of the trace elements (Bartlett 1999). The statistical analyses also suggested that abundant bioactive metals strongly interacted and/or influenced the mobility and partitioning of unwanted metal ions, namely, Pb and Cr, available in the ambient environment.

**Table 3** Decline of the elemental concentrations in the canal from site 1/2 to site 4

Elements	Wastewater			Bottom sediment		
	Highest conc.	Lowest conc. (at site 4)	% reduction	Highest conc.	Lowest conc. (at site 4)	% reduction
S	4,439.0 <sup>a</sup>	1,211.1	73	37,544.4	12,711.4	66
Ca	241.2	94.4	61	110,078.9 <sup>a</sup>	9,348.4	91
Cr	3.2 <sup>a</sup>	0.11	96	15,561.1 <sup>a</sup>	861.6	94
Mn	11.7	2.2	81	481.8	233.8	51
Fe	3.3 <sup>a</sup>	0.83	75	27,110.8	18,980.3	30
Ni	0.45 <sup>a</sup>	0.16	64	105.9	29.1	73
Cu	0.39	0.18	54	212.1	117.7	45
Zn	3.2	1.6	46	621.1	258.4	58
Rb	0.48	0.15	67	175.5	121.7	31
Sr	0.57	0.21	59	131.8 <sup>a</sup>	58.5	55
Pb	1.5 <sup>a</sup>	0.17	88	241.9	93.5	61

<sup>a</sup>Values were recorded at site 1

Significant decrease in the metal content of both water and sediment along the course of the canal was evident from the study (Table 3), indicating natural amelioration of waste metals. Most of the elements were ameliorated within the stretch of the 30–32-km journey of the canal (sites 1/2 to site 4). As for example, the average decline of elemental concentration in water of site 4, 96% for Cr, 88% for Pb, 81% for Mn, and in bottom sediment at site 4, 94% for Cr, 91% for Ca, 73% for Ni, was recorded. It was interesting to note that the concentration levels of different elements at site 4 near the confluence with the Kultigong river were well below and/or comparable to the safe limits formulated by the Central Pollution Control Board ([www.envfor.nic.in/cpcb](http://www.envfor.nic.in/cpcb)), India (as for example, 5.0 mg L<sup>-1</sup> for Zn, 3.0 mg L<sup>-1</sup> for Cu, 2.0 mg L<sup>-1</sup> for Mn, 3.0 mg L<sup>-1</sup> for Fe, and 0.10 mg L<sup>-1</sup> for Pb). The inherent quality of the wetlands for treatment and improvement of water quality was pointed out by other workers (Reed 1991).

**Conclusion**

Different components of the East Calcutta Wetlands were exhibiting the attribute to deal with broad spectrum of industrial contaminants, especially waste metals. The capacity to trap and efficient modification of different metals throughout the year were cursors of the wetlands’ characteristics acting as the “kidney of nature.” Numerous studies have shown that wetlands can

be effective tertiary processors of wastewater effluent, and the present study on ECW attests the same. It was recorded in the study that the significant decrease taking place in the metal content of both water and sediment along the study site of the wastewater-carrying canal assert the role of wetlands in wastewater remediation (Zhang et al. 1997). The load of most of the unwanted metals in the effluent was significantly reduced within the stretch of the 30–32-km seaward journey of the canal. Day et al. (2004) pointed out the use of wetlands for treatment of wastewaters with a number of ecological and economic benefits. Natural stabilization of both composite industrial effluents mixed with municipal wastewater by the wetland areas was recorded to be more efficient to that established by an effluent treatment plant (ETP). Chattopadhyay (2002) studied the changes of oxygen status in stabilization pond in an isolated, well-defined, and established large tannery ETP in Bihar, known to be the best in India. He recorded the reduction of 5-day biochemical oxygen demand and chemical oxygen demand values in the stabilization pond after secondary treatment in that ETP to the extent of 91.94% and 31.75%, respectively, as against the raw composite tannery effluent, while, similarly, in ECW a reduction of 82% and 79%, respectively, was estimated, comparing the raw influent wastewater and the wastewater at final discharge site at Kultigong river (site 4). In 1945, the total wetland area was 81 km<sup>2</sup> which had been decimated today to 51 km<sup>2</sup>. Even after the crunch of nearly 37% of wetland area, ECW had therefore an inherent

property to ameliorate the metal contamination and improve the water quality, acting as a money and energy saver of the region. Of late, the entire area has been declared as a Ramsar Site, a very positive protective step to conserve wetlands of importance. At present, motivated conservation efforts can only resist the further crunch of this immensely productive and excellently effective natural ETP in Calcutta's own backyard.

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