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Ecological Risk Assessment of Metals Contamination in the Sediments of Natural Urban Wetlands in Dry Tropical Climate

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Abstract The pollution load due to metal contamination in the sediments of urban wetlands (Dhanbad, India) due to illegal release of domestic and industrial wastewater was studied by using various geochemical indices, such as contamination factor (C_f), degree of contamination (C_d), modified degree of contamination (mC_d), pollution load index (PLI) and geoaccumulation index (I_{geo}) for Cu, Co, Cd, Cr and Mn. Cluster analysis (CA) and Principal component analysis (PCA) of metals present in wetland sediments were carried out to assess their origin and relationship with each other. The C_f values for different metals in the wetlands under investigation indicated low to very high level of pollution (C_f ranged between 0.02 and 14.15) with highest C_f (14.15) for Cd. The wetland receiving both domestic and industrial wastewater had the highest values of C_d, mC_d and PLI as 17.48, 3.49 and 1.03 respectively.

Keywords Contamination factor · Degree of contamination · Geoaccumulation index · Pollution load index

Wetlands offer important ecosystem services such as water purification, filtration, retention of nutrients, flood control, ground water recharge, and providing habitat for a variety of species (Boyer and Polasky 2004). Pollution threats of metal contamination in aquatic environments have been a pervasive problem globally due to their toxicity, abundance, persistence and bioaccumulation (Niu et al. 2015; Wali et al. 2015). Municipal and industrial wastewaters act as sources of heavy metals (Abdel-Khalek 2015; Kumari and Tripathi 2015) which contaminate natural urban wetlands of the aquatic ecosystem. The metal contamination in wetland sediments tends to increase due to the accumulation of metals in the sediment and then enters into the food chain by transferring to higher trophic levels (Çevik et al. 2009, Naccari et al. 2015). High concentrations of various heavy metals such as Cd, Hg, Pb, Cr, etc. adversely influences nervous, cardiovascular, respiratory, gastrointestinal, hepatic, renal, hematopoietic, immunological and dermatological systems (Shrivastava et al. 2002; Vukićević 2012; Rice et al. 2014). The natural wetlands under study are habitats and food sources to various aquatic organisms and a significant income for the nearby population, so there is a strong need to assess the heavy metal load in these urban wetlands to prevent the intrusion of toxic metals into urban aquatic ecosystems and food cycle.

The main objectives of the present study were to assess the concentrations of trace metals Cu, Cd, Mn, Cr and Co in the surface sediments of contaminated urban wetlands; and to evaluate sediment toxicity and ecological risk of heavy metals to the urban wetland ecosystem of Dhanbad, an industrial coal city in India using various geochemical indices.

Materials and Methods

The natural urban wetlands situated across industrial Dhanbad city (known as Coal capital of India) were selected for assessing the risk to the concerned ecosystem services in these aquatic bodies whose characteristics are shown in Fig. 1 and Table 1.

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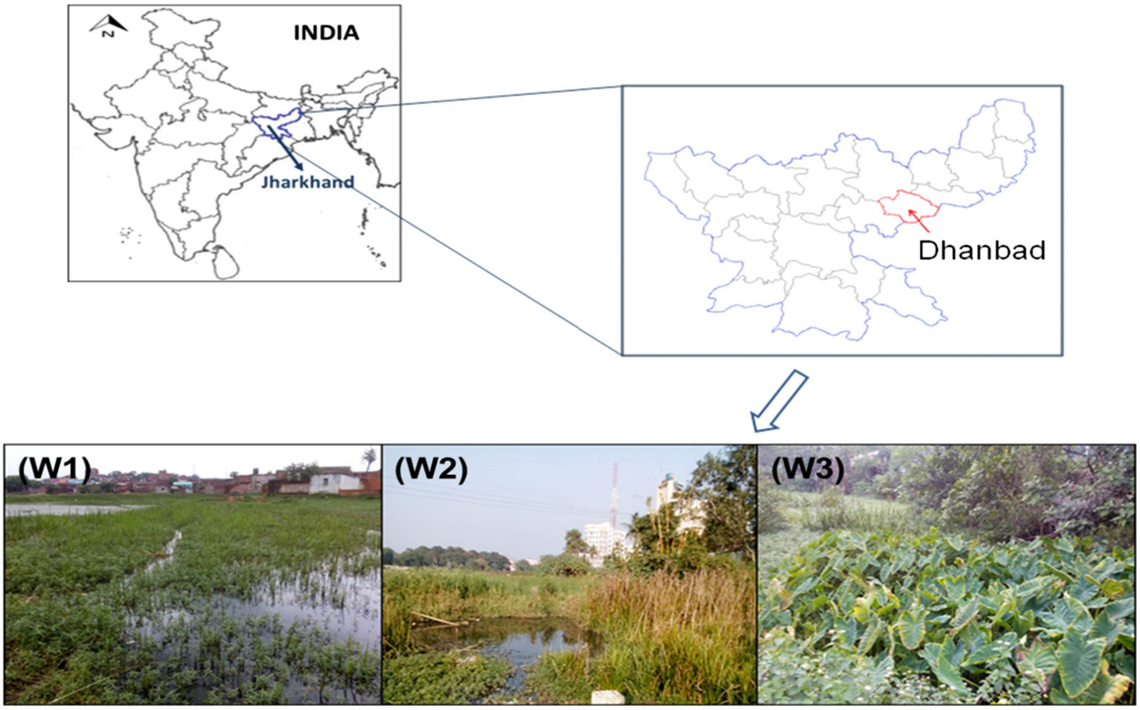

Fig. 1 Location map showing natural urban wetlands situated in Dhanbad city in the Indian state of Jharkhand which received domestic and industrial wastewater generated in their vicinity and heavy metals accumulated in sediments. Wetland (W1) receiving domestic sewage is dominated by *Scirpus grossus* with co-existence of *Eichhornia crassipes*; Wetland (W2) receiving industrial and domestic wastewater is dominated by *Typha latifolia;* and Wetland (W3) receiving domestic sewage is dominated by *Colocasia esculenta, Eichhornia crassipes* and *Monochoria hastata*

Table 1 Characteristics of degraded urban wetlands

Characteristics	Wetland 1(W1)	Wetland 2(W2)	Wetland 3(W3)
Geographical location	23°48′12.79″N, 86°25′4.45″E	23°47′57.74″N, 86°38′9.66″E	23°48′16.04″N, 86°25′17.77″E
Vegetation	*Scirpus grossus* was seen as the dominant plant species with existence of *Eichhornia crassipes* and some other floating macrophytes such as duckweeds. The cultivation of water caltrop by local people was also observed	*Typha latifolia* (cattail) was seen as the dominant plant species due to its high metal tolerance ability	*Colocasia esculenta, Eichhornia crassipes*, *Monochoria hastata* were seen with other aquatic weeds
Source(s) of pollution	Domestic wastewater	Domestic + industrial wastewater	Domestic wastewater
Ecological risks	Bioaccumulation of metals in food chain and toxicity to aquatic plants and animals	Incorporation of metal pollution to nearby water bodies, loss of habitat of birds	Intrusion of metals in food chain and their toxicity to aquatic plants and animals

The climate of Dhanbad city is transitional between humid subtropical climate and a tropical wet and dry climate, characterized by a rainy season between June to October (average annual rainfall: 1241 mm) with a hot season from March to May (peak temperature reaches 48°C).

A total of ten sediment samples (depth: 0–15 cm) from each wetland were collected into polyethylene zipper bags and transported to the laboratory for further analysis. The collected sediments were air dried and ground into powder with the help of a mortar and pestle and then sieved (<2 mm) for the determination of physico-chemical properties of the collected sediments. A portion of 0.5 g of sediment was digested using 10 mL of HNO_3 (69 %; EMPARTA) and HCl (~37 %; EMPARTA) (3:1) (Maiti and Nandhini 2006) over a hot plate (90°C) gently until the escape of NO_2 fumes ceased and the solution becomes clear. Then 1 % HNO_3 solution was added to the digested mass to make up a volume of 50 mL and filtered using Whatman #42 filter, pore size 2.5 µm. The samples were refrigerated until analysis (Kumar and Maiti 2014) for the determination of metals (Cu, Co, Cd, Cr and Mn) concentration using flame atomic absorption spectrophotometer (FAAS-GBC Avanta, Australia). The detection limits were 0.001 mg kg^{-1} for Cu, 0.004 mg kg^{-1} for Co, 0.0004 mg kg^{-1} for Cd, 0.0030 mg kg^{-1} for Cr and 0.0015 mg kg^{-1} for Mn. The pH and electrical conductivity were measured in a soil–water suspension (1:2.5; soil: deionized water) using a pH meter (Cyberscan 510) and conductivity meter (EI 601) respectively; organic carbon (Walkley and Black 1934); available phosphorus (Olsen et al. 1982); available nitrogen (Subbiah and Asija 1956), exchangeable potassium was extracted by neutral 1 N ammonium acetate solution (1:10; w/v) and determined by flame photometer (Jackson 1973).

In order to assess the pollution level in these urban wetlands, various geochemical indices were used such as contamination factor (C_f), degree of contamination (C_d), modified degree of contamination (mC_d), pollution load index (PLI) and geoaccumulation index (I_{geo}).

1. Contamination factor (C_f)

The contamination factor (C_f) for different metals was calculated by the formula given by Hakanson (1980):

$$C_f = \frac{C_{metal}}{C_{background}}$$

where, C_{metal} = total concentration of metal in the sediment (in mg kg^{-1}); $C_{background}$ = background metal concentration in unpolluted sediment (in mg kg^{-1}).

2. Degree of contamination (C_d)

The overall degree of contamination (C_d) was calculated as per equation given by Hakanson (1980):

$$C_d = \sum_{i=1}^{n} C_f^i$$

C_f and C_d were classified into seven categories as shown in Table 2.

3. Modified degree of contamination (mC_d)

Table 2 Contamination categories based on values of C_f and C_d (Vaezi et al. 2015)

C_f	C_d	Description
$C_f < 1$	$C_d < 7$	Low
$1 < C_f < 3$	$7 < C_d < 14$	Moderate
$3 < C_f < 6$	$14 < C_d < 28$	Considerable
$C_f > 6$	$C_d > 28$	Very high

In the present study, the modified degree of contamination (mC_d) as defined by Abrahim and Parker (2008) is used:

$$mC_d = \frac{\sum_{i=1}^{n} C_f^i}{n}$$

where, n represents the total number of metals taken under consideration.

The modified degree of contamination consists of four categories as shown in Table 3.

4. Pollution load index (PLI)

Pollution load index (PLI) was used by Tomlinson et al. (1980) to assess the extent of the metal contamination in marine sediments. PLI was calculated as follows:

$$PLI = \left(C_{f1} \times C_{f2} \times C_{f3} \times \ldots\ldots \times C_{fn}\right)^{(1/n)}$$

where, C_f is the contamination factor and n is the number of metals. PLI value >1 indicates pollution whereas PLI value <1 indicates no pollution.

5. Geo-accumulation index (I_{geo})

The degree of contamination in wetland sediments can be assessed by calculating geo-accumulation index (I_{geo}) given by the following equation (Vaezi et al. 2015):

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right)$$

where, C_n is the concentration of metals in the sediments in mg kg^{-1} and B_n is the geochemical background concentration of the metal (in mg kg^{-1}). A constant 1.5 is involved to take the lithological variability in the sediments into account (Abrahim and Parker 2008). The geo-accumulation index has seven classes defined as follows as shown in Table 4.

The metal concentrations in the wetland sediments are reported in mg kg^{-1} of the sediment. Differentiations between wetlands with respect to sediment properties and mean metal concentrations were evaluated by using a one

Table 3 Contamination categories based on mC_d values (Abrahim and Parker 2008; Vaezi et al. 2015)

mC_d	Description
$mC_d < 1.5$	Zero to very low degree of contamination
$1.5 < mC_d < 2$	Low degree of contamination
$2 < mC_d < 4$	Moderate degree of contamination
$4 < mC_d < 8$	High degree of contamination
$8 < mC_d < 16$	Very high degree of contamination
$16 < mC_d < 32$	Extremely high degree of contamination
$mC_d \geq 32$	Ultra high degree of contamination

Table 4 Contamination categories based on I_{geo} values (Machender et al. 2013; Kumar and Maiti 2015)

I_{geo}	Description
>5	Extremely polluted
4–5	Strongly to extremely strongly polluted
3–4	Strongly polluted
2–3	Moderately to strongly polluted
1–2	Moderately polluted
0–1	Unpolluted to moderately polluted
≤0	Unpolluted

way analysis of variance (ANOVA). Duncan's Multiple Range Test (DMRT) post hoc analysis at $p < 0.05$ was performed to define which specific mean pairs significantly differed. Hierarchical cluster analysis (CA) was performed on the normalized dataset of metals using average linkage (between groups) with Euclidean distances as measure of similarity. Principal components analysis (PCA) was performed for the metal concentration in wetland sediments to discriminate the sources of metal pollution as natural and anthropogenic (Sakizadeh et al. 2015). Normalized variables (original variables) were transformed into the rotated components to extract the significant principal components (reduction in contribution of insignificant variables). Further, these principal components were subjected to Varimax rotation to generate PC factors. All statistical calculi were performed using software SPSS, IBM statistics version 16.0 package and graphs were prepared using software Origin 8.

Results and Discussion

Collected sediments from the three urban wetlands were characterized based on their physico-chemical properties as shown in Table 5. The organic carbon and organic matter content in the three wetlands under study ranged between 1.59 %–2.52 % and 2.74 %–4.35 % respectively. The sediments of W2 were found neutral whereas the sediments of W1 and W3 were found to be slightly acidic. The wetlands can be considered as phosphorus deficient due to phosphorus concentration below 8 mg kg^{-1}.

The metal concentrations (Cu, Cd, Mn, Cr and Co) in the sediments of the three wetlands are shown in Table 6. Cu, Cd and Cr were found highest in W2 with concentrations of 97.89 mg kg^{-1}, 2.83 mg kg^{-1} and 12.27 mg kg^{-1} respectively however highest Co concentration (16.78 mg kg^{-1}) and Mn concentration (401.2 mg kg^{-1}) were present in W1 and W2 respectively.

The C_f of different metals in the three wetlands with respect to the background concentrations of metals of those respective metals present in the earth's shale (Salomons and Förstner 2012) are shown in Table 7. Based on the C_f values, the pollution level by various metals ranged between low to very high. However, the C_d and mC_d values of metal contamination in the wetlands indicated moderate level of metal pollution. The PLI value of W2 was found >1 indicating significant metal pollution (Table 7). The pollution level in sediments of W2 can be interpreted as the highest amongst the wetlands considered in the present study with highest values of C_d, mC_d and PLI as 17.48, 3.49 and 1.03 respectively.

The geoaccumulation index of various metals with respect to the background concentration was calculated as shown in Fig. 2. The I_{geo} values of Mn exhibited values that were in the moderately to strongly polluted category (i.e., I_{geo}: 1–2 and I_{geo}: 2–3). I_{geo} value of Cu (0.53) in W2 has shown unpolluted to moderate pollution.

Hierarchical cluster analysis (CA) is a statistical method to identify the group of samples that behave similarly. The cluster as shown in Fig. 3 has two bigger sub-groups: the first group contains Cd, Cr, Co and Cu (anthropogenic origin) whereas the second one includes Mn (natural origin). Further, the results also revealed that Cr and Cd are closely related to each other which arise from anthropogenic sources. Moreover, Co, Cr and Cd are elements of the same group (group I) which strongly correlate with the

Table 5 General properties of sediments collected from urban wetlands (Mean ± SD) (n = 10)

Parameter	Unit of measurement	W1	W2	W3
pH_{H2O} (1:2.5)(w/v)	–	6.62 ± 0.51^b	7.2 ± 0.35^a	5.54 ± 0.66^c
EC(1:2.5) (w/v)	µS/cm	450.6 ± 70.65^c	836.1 ± 137.8^a	734.2 ± 53.79^b
Organic carbon	%	1.59 ± 0.19^c	2.12 ± 0.10^b	2.52 ± 0.31^a
Organic matter	%	2.74 ± 0.33^c	3.65 ± 0.18^b	4.35 ± 0.54^a
Available N	mg kg^{-1}	208.88 ± 1.84^b	331.1 ± 2.57^a	116.48 ± 3.89^c
Available P	mg kg^{-1}	3.17 ± 0.25^c	6.71 ± 0.42^a	3.62 ± 0.29^b
Exchangeable K	mg kg^{-1}	40.14 ± 5.14^b	46.75 ± 9.69^a	11.47 ± 4.23^c

W1, W2 and W3 represent contaminated urban wetlands. *Different alphabetical letters* in the same row indicates significant difference at $p < 0.05$ according to Duncan's multiple range test

Table 6 Metal concentration (in mg kg^{-1}) present in the sediments of urban wetlands (Mean ± SD) (n = 10)

Metals	W1	W2	W3	BC*
Cu	59.16 ± 7.01[b] (50.3–71.8)	97.89 ± 7.84[a] (87.6–108.2)	37.23 ± 5.11[c] (32.1–48.0)	45
Cd	2.04 ± 0.30[b] (1.4–2.4)	2.83 ± 0.29[a] (2.5–3.3)	1.98 ± 0.30[b] (1.5–2.4)	0.2
Mn	243.65 ± 17.30[c] (208.6–263.4)	311.99 ± 19.62[b] (286.2–354.5)	401.2 ± 17.58[a] (378.1–426.8)	600
Cr	5.85 ± 0.84[b] (4.4–6.7)	12.27 ± 1.44[a] (10.2–15.2)	2.24 ± 0.81[c] (1.6–4.4)	83
Co	16.78 ± 3.95[a] (11.2–24.2)	9.34 ± 1.58[c] (6.4–11.2)	12.34 ± 0.92[b] (10.8–13.8)	19

* Background metal concentration in earth's shale (Salomons and Förstner 2012). *Different alphabetical letters* in the same row indicates significant difference at $p < 0.05$ according to Duncan's multiple range test, metal concentration in *brackets* represents the range

Table 7 Metal contamination factors, degree of contamination, modified degree of contamination and pollution load index for each wetland

Contamination factors based on average shale content						All elements		
Wetland	Cu	Cd	Mn	Cr	Co	C_d	mC_d	PLI
W1	1.31	10.20	0.40	0.07	0.88	12.87	2.57	0.80
W2	2.17	14.15	0.51	0.14	0.49	17.48	3.49	1.03
W3	0.82	9.90	0.66	0.02	0.64	12.07	2.41	0.62

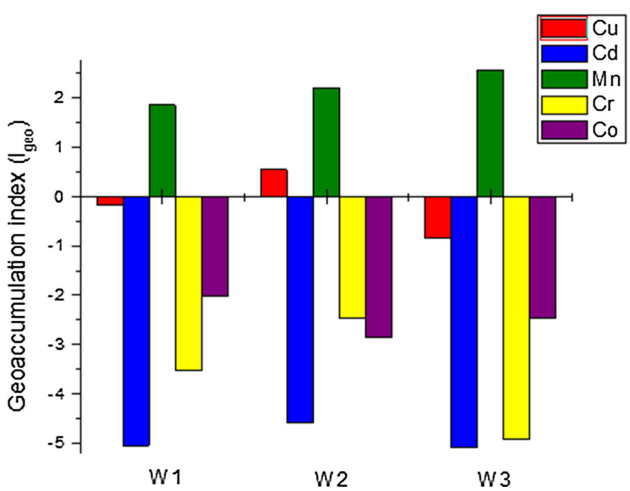

Fig. 2 Geoaccumulation index of various metals present in the sediments of urban wetlands

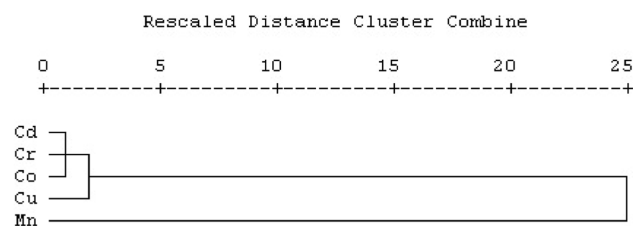

Fig. 3 Dendrogram using average linkage (between groups) showing hierarchical clustering of different metals present in the sediments of urban wetlands

alumino-silicate phases, thus indicating slight natural origin of Co along with Cr and Cd. Mn did not show any similarity with other metals showing its natural origin in wetlands.

Principal component analysis (PCA) has revealed that two principal components were extracted, together explaining approximately 88.13 % (PC1: 59.38 %; PC2: 28.74 %) of the information contained in the initial variables. The location of metals in the plane of coordinates formed by the two new components, PC1 and PC2, is shown in Fig. 4.

The metals were distributed into three groups, containing Co (Group I), Mn (Group II) and Cr, Cd and Cu (Group III). PC1 separated Group I and II containing Co and Mn (negative region of PC1) from Group III (containing Cr, Cd and Cu). It can be inferred from the complementary results of PCA and CA that Cr and Cd are closely related to each other and result from the same anthropogenic source.

The results of the present study enhanced our knowledge about the levels and sources of heavy metals in the sediments of natural wetlands situated in industrialized cities. The various geochemical indices show metal contamination in these wetlands and an increase in the pollution was observed with closeness to industrial sources. High level of metal contamination was observed in wetland 2 (W2). The

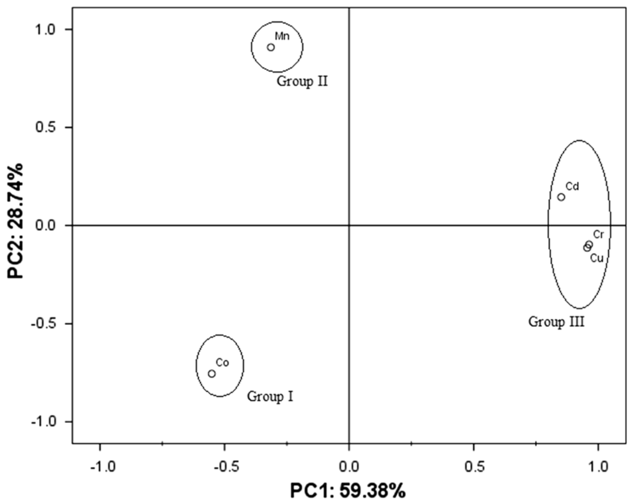

Fig. 4 Principal component analysis for the heavy metals in urban wetland sediments

possible reason for high metal contamination in W2 could be proximity to (i) industrial effluent discharge from nearby coke oven plants and briquettes industries; and (ii) domestic sewage from nearby residential establishments. Manganese was found high in all the sediments due to its abundance in the earth's shale. Cadmium was found significantly above the usual concentration present in the earth's shale. This indicates the incorporation of Cd into wetland ecosystem due to anthropogenic activities. These wetlands acted as purification systems for the metals to be discharged into the water streams further. One of the wetlands (W2) was situated across the tributaries of Damodar which is an important river of Jharkhand, India. This wetland helps in dampening the metal load on Damodar river. The present study enables us to practice mitigation measures for restricting the release of heavy metals into these wetlands for avoiding their intrusion into aquatic ecosystem and food chain.

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