Temporal changes and depth wise variations in pit pond hydrochemistry contaminated with industrial effluents with special emphasis on metal distribution in water–sediment system

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ABSTRACT

The investigation showed pronounced temporal and vertical variations of pit lake-water chemistry contaminated with industrial effluents. An intermixing layer of few meters at a depth of 5–8 m usually separates an upper oxic epilimnion with alkaline pH from deeper sub-oxic/anoxic zone with relatively lower pH. Metal concentrations were in higher magnitude at anoxic zone in comparison to surface layer. Most of the parameters including metals showed higher concentrations during summer, while least concentrations were observed during monsoon. In shallow sediments, metals were mainly in insoluble-residual form, while redox metals were fractionated as oxihydroxide-reducible form. Geoaccumulation of metals in bottom sediments were Fe > Cr > Pb > Cu > Cd > Mn > Zn. Toxicity assessment showed that pit pond water is highly contaminated (C_d = 7.52) and moderate pollution load (PLI = 2.272) in shallow sediments, with metal evaluation index (HEI) value of 11.08 and 15.91 respectively.

1. Introduction

Contamination of surface water due to wastewater discharge is of major environmental concern and was reported by several earlier workers [1–5]. Industrial effluents contain appreciable amounts of metals, and their long term continuous discharge into the water body results elevated metal concentrations in water and sediments. Even though the metals are present in dilute, undetec quantities, their recalcitrance and consequent pertablesistence in water bodies imply that through natural processes, concentrations may become elevated to such an extent that they begin to exhibit toxic characteristics [6]. Pit lakes are characterized to have their own metal load due to pre mining activity. The hydrogeochemistry of pit lakes were studied by several earlier workers [7–10], but literature on contamination of pit lake due to industrial wastewater discharges are very few. Parshley and Bowell [11], Gammons and Duaime [12] demonstrated the long term geochemical behavior of pit lake water and how the complex limnology can affect the seasonal water quality. Depending on chemical and geological conditions, heavy metals can be partitioned into different chemical forms that are associated with a variety of organic and inorganic phases [13]. Sediments act as both carriers and sink for contaminants in aquatic environment and the potential risk of metals in water–sediments is associated with both their total content and their speciation [14,15].

Field study for this research work was conducted at Mangalpur industrial area (Latitude 23°37′N and Longitude 87°08′E) of Raniganj coal-field belt, an extension of Chotonagpur platue, situated at western part of state West Bengal, India. This area is famous for containing valuable coal deposit of sub bituminous type and possesses open cast mining activity. After end of mining, the abandoned pits are filled up by water (through precipitation and groundwater influx) and converted into open cast pit pond (OCP). Mangalpur industrial area altogether has five Sponge iron and Ferro alloy industries with their captive power plants. Effluents generated by this industries released through a commonly united open channel and terminated into the OCP having surface area of about 64,000 sqm. There were previous investigations on characterization of industrial effluents and its effects on receiving pit pond water [5,16], but the previous investigations were excluded of detail hydro-geochemical survey of the pit lake.

The present investigation deals with (1) temporal and depth wise variations in hydrochemistry of OCP water, (2) distribution of metals in water–sediment system, and (3) contamination assessment of pit pond by using various indices.

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2. Experimental methodology

2.1. Water samples collection and analysis

Effluents samples were collected from industrial discharge point as well as from different points of effluents channel. OCP water samples were collected from the different sites of OCP. Water samples from different depth zone of OCP were collected by specially designed battery driven peristatic pump connected with a long narrow flexible tube at one end. Water and wastewater samples are collected in wide mouth plastic bottles. Water pH, conductivity (EC) and dissolved oxygen (DO) were measured in the field by using hand analyzer pH, Conductivity and DO meter.

The effluents and OCP samples were acidified with 0.5 ml of concentrated HNO_3 to prevent the precipitation of metals, and freeze for further physico-chemical analysis. The samples preservation and analysis were performed according to Standard methods, APHA [17]. For the estimation of metals, the water and wastewater samples were digested with 10 ml concentrated HNO_3, filtered and analyzed for Fe, Cr, Cd, Pb, Mn, Zn, Cu in AAS (GBC Avanta).

2.2. Analysis of shallow sediments samples

Sediments of water body act as sinks for pollutant precipitation and are important for assessment of ecological status of water body. Due to limited scope of study, shallow sediments samples (depth of 5 m) were collected from different sites of contaminated pit pond banks. Though metal content of shallow sediments did not represent the quantitative view of metal precipitation, but it provides an apparent view of metal contamination in pit pond sediments due to industrial discharge. Sediments samples were air dried and analyzed for pH, and electrical conductivity (EC) as per standard methods, APHA [17]. Total organic matter (OM) was determined by wet oxidation [18]. Cation exchange capacity (CEC) was carried out as the total basic cations extracted with 1 (M) CH_3COONH_4 [19].

For estimation of heavy metals, 1 g of sediment samples (DW) were digested with a mixture of concentrated HNO_3 and $HClO_4$ (4:1) [20]. The solution was filtered and the clear solution was analyzed for total Fe, Cr, Cd, Pb, Mn, Zn, Cu content in sediment samples. Metal fractionations in OCP sediments were estimated by sequential extraction process as per modified BCR sequential extraction procedure [21]. The extractant and digested solutions were diluted with distilled water to the desired dilution factor and estimated in AAS.

As there was no previously recorded background values for metal content before these industries were set up, therefore a set of control water and sediments samples were collected from nearby uncontaminated OCP which is devoid of any type of industrial discharge and treated as background reference value.

2.3. Index for assessing metal contamination in water and sediments

Contamination index (C_d) [22] is used to measure the quality of water. The (C_d) is computed separately for each metal, as a sum of contamination factors (C_f) of individual elements exceeding the permissible limits. The contamination index is calculated from the equation below

$$C_d = \sum_{i=1}^{n} C_f, \qquad \text{where } C_f = \frac{\text{Analytical value for } i\text{th component}}{\text{Permissible limits for } i\text{th component}}$$

The index of geoaccumulation (I_{geo}) enables the assessment of metal accumulation in bottom sediments by comparing present and pre industrial concentration [23].

$$I_{geo} = \log_2 \frac{C_n}{1.5 B_n}$$

where C_n is the measured metal concentrations in sediment fraction (<2 μm) and B_n is the geochemical background value of metals. The factor 1.5 is introduced to include possible variations of background value due to natural fluctuations.

Pollution load index (PLI) [24] has been calculated to determine the pollution load of shallow sediments at contaminated site. PLI is represented as geometric mean of C_f value of n number of metals estimated at contaminated site. The index is based on the concentration factor (C_f) of each metal present in the soil.

$$C_f = \frac{H_c}{H_b}$$

where H_c is the metal concentration at contaminated site and H_b is the maximum permissible limits/background value of metals.

Heavy metal evaluation index (HEI) [25] gives an overall quality of the water–sediments with respect to heavy metals. HEI is computed as

$$\text{HEI} = \sum_{i=1}^{n} \frac{Hc}{Hmax}$$

Hc is the experimental value of ith parameter at contaminated site and Hmax is the maximum admissible concentrations of ith parameter or its background reference value.

2.4. Quality control assurance

Care has been taken for sample collection and preservation during every experimental procedure, and for the analytical precision, each (water and sediments) samples were performed for three replicates. E-mark (AR grade) standards were used for the preparation of standard curve during analysis of metals. For further enhancement of experimental results, only the mean values for each parameter along with standard deviation (SD) were considered.

2.5. Statistical analysis

Correlations study was performed for different water parameters (excluding metals) for analyzing the interrelations between them. Factor analysis is used here as a numerical method of discussing variables and identifying geochemical processes by extracting minimum acceptable eigen value greater than 1. Principle Component Analysis (PCA) along with varimax rotation was performed for physico-chemical parameters of OCP water and sediments to analyzed the interrelated variations and also identify their possible source. Regression analyses (R^2) were performed between metal content in water with sediment metal concentrations. Pearson's correlations (r) was performed between C_f value of metals (both water and sediments) with metal I_{geo} value for the better interpretation/understanding of metal accumulation, distribution and their interrelations in water–sediment system. Statistical calculations are carried out at significance level 0.05 by XL Stat (version 10).

3. Results and discussion

3.1. Characterization of industrial effluents and receiving pit pond water

The effluent generated by these industries is released into a nearby open cast pit pond (OCP) through a commonly united open

Table 1
Characterization of effluents from Sponge iron industries.

Physico-chemical parameters	Effluents from Sponge iron and Ferro allow industries [a,b]	IS effluents discharge standards for surface water [c]
pH	8.94–8.36 ± 0.24	5.5–9.0
EC (ms 25 °C)	21.8–12.27 ± 4.19	–
TSS (μg L^{-1})	1516–1075 ± 64.23	100
DO	3.14–2.34 ± 0.11	–
BOD	3.64–2.26 ± 0.61	30
COD	222–152 ± 30.26	250
TH	643–590 ± 21.64	600
PO_4^{3-}-P	0.138–0.104 ± 0.012	5.0
NO_3^--N	0.256–0.174 ± 0.04	18
SO_4^{2-}	201.7–161.4 ± 17.08	1000
Cl^-	64.8–42 ± 8.32	1000
Na^+	66–54 ± 4.76	–
K^+	19–11.5 ± 3.64	–
Fe	8.62–7.23 ± 0.58	3.0
Cr	0.832–0.692 ± 0.06	2.0
Cd	0.034–0.024 ± 0.005	2.0
Pb	0.366–0.272 ± 0.039	0.1
Mn	0.774–0.689 ± 0.040	2.0
Zn	0.716–0.672 ± 0.021	5.0
Cu	0.763–0.704 ± 0.025	3.0

Except pH, EC and TSS, other parameters expressed as mg L^{-1}

[a] Gupta et al. 2008 [5].
[b] Nayek et al. 2010 [16].
[c] Indian standards – IS 2490 Part I: 1981 [26].

channel without any proper treatment. Previously it was shown [5,16] that industrial effluents as well as OCP waters are contaminated with heavy and trace metals. Effluents released by industries was alkaline in nature (Table 1) with high suspended solids (TSS), total hardness (TH) and chemical oxygen demand (COD), of which TSS and TH value exceeded the IS industrial effluents discharge standards for surface water [26]. Effluents showed less amounts of dissolved oxygen (DO) and biodegradable pollutants (BOD) with very poor PO_4^{3-}-P and NO_3^--N concentrations; while SO_4^{2-} and Cl^- content were in moderate range. Among the studied metals Fe concentration was much higher, and Fe and Pb content in industrial effluents exceeded the Indian Standards [26] for dis-

charge into inland surface water. Contaminated OCP water showed slightly alkaline pH with moderate DO and BOD (Table 2). Total dissolved solids (TDS), COD and TH were higher in comparison to uncontaminated pond but well under the recommended irrigation standards [27,28]. PO_4^{3-}-P and NO_3^--N concentrations in OCP water were much low with higher SO_4^{2-} and Cl^- content. Metal concentrations in contaminated OCP water were noticeably higher in comparison to uncontaminated pit lakes. Cr and Mn content in OCP water exceeds the FAO Standards for agricultural application [27], but the values were very much within the recommended IS irrigation standards [28]. The values for most of the parameters in the contaminated water body were found to be much lower

Table 2
Temporal variations in hydrochemistry of contaminated pit pond.

Water parameters	Contaminated pit pond			Uncontaminated pit pond (Max-Min ± SD)	IS standards for irrigation [a]	FAO irrigation standards [b]
	Summer (2007–2009)	Monsoon (2007–2009)	Winter (2007–2009)			
Temp (°C)	27.80 ± 0.63	22.50 ± 1.68	14.00 ± 0.82	26.4–27.8 ± 0.58	–	-
pH	8.15 ± 0.21	7.53 ± 0.14	7.87 ± 0.06	6.8–7.7 ± 0.37	5.5–9.0	6.5–8
EC (ms 25 °C)	5.90 ± 0.45	8.26 ± 1.85	5.10 ± 0.85	4.32–6.12 ± 0.77	–	750–2000
TDS (μg L^{-1})	361.50 ± 13.30	379.00 ± 25.22	270.50 ± 43.09	74–92 ± 7.83	2100	2000
DO	6.95 ± 0.44	9.75 ± 0.96	7.20 ± 0.45	7.8–10.2 ± 1.02	–	–
BOD	5.48 ± 0.63	7.00 ± 0.82	5.68 ± 0.57	4.8–6.2 ± 0.59	100	–
COD	127.75 ± 11.09	113.00 ± 10.00	127.75 ± 8.18	42–56 ± 6.61	–	–
TH	246.00 ± 19.11	221.00 ± 11.94	240.00 ± 14.13	126–144 ± 7.55	–	–
HCO_3^-	3.68 ± 0.043	3.44 ± 0.06	3.63 ± 0.07	2.86–3.22 ± 0.15	–	600
PO_4^{3-}-P	0.06 ± 0.02	0.05 ± 0.012	0.06 ± 0.013	0.196–0.228 ± 0.02	–	–
NO_3^--N	1.16 ± 0.24	1.18 ± 0.05	0.62 ± 0.60	0.674–0.872 ± 0.08	18	–
SO_4^{2-}	118.88 ± 5.33	98.00 ± 12.44	117.50 ± 12.18	66.4–79.2 ± 5.48	1000	1000
Cl^-	36.00 ± 3.92	27.00 ± 3.92	31.25 ± 3.77	0.11–0.18 ± 0.03	600	1100
Na^+	36.46 ± 3.21	28.00 ± 4.69	33.30 ± 4.30	39.2–44.05 ± 2.12	–	–
K^+	8.05 ± 0.33	6.92 ± 0.29	6.88 ± 0.25	6.26–8.2 ± 0.84	–	–
Fe	0.152 ± 0.02	0.108 ± 0.013	0.126 ± 0.008	0.026–0.035 ± 0.004	3.0	5.0
Cr	0.783 ± 0.06	0.550 ± 0.057	0.692 ± 0.014	0.037–0.048 ± 0.005	–	0.1
Cd	0.006 ± 0.001	0.005 ± 0.001	0.006 ± 0.001	ND	–	0.01
Pb	0.023 ± 0.01	0.022 ± 0.004	0.021 ± 0.003	ND	–	5.0
Mn	0.386 ± 0.03	0.299 ± 0.036	0.328 ± 0.034	0.024–0.036 ± 0.005	2.0	0.2
Zn	0.218 ± 0.04	0.158 ± 0.035	0.198 ± 0.034	0.018–0.024 ± 0.003	–	2.0
Cu	0.145 ± 0.03	0.065 ± 0.067	0.118 ± 0.033	Trace–0.0012 ± 0.001	–	0.2

Except pH, EC and TDS, other parameters expressed as mg L^{-1}, ND, not detectable.

[a] Indian standards – IS 11624: 1986 [28].
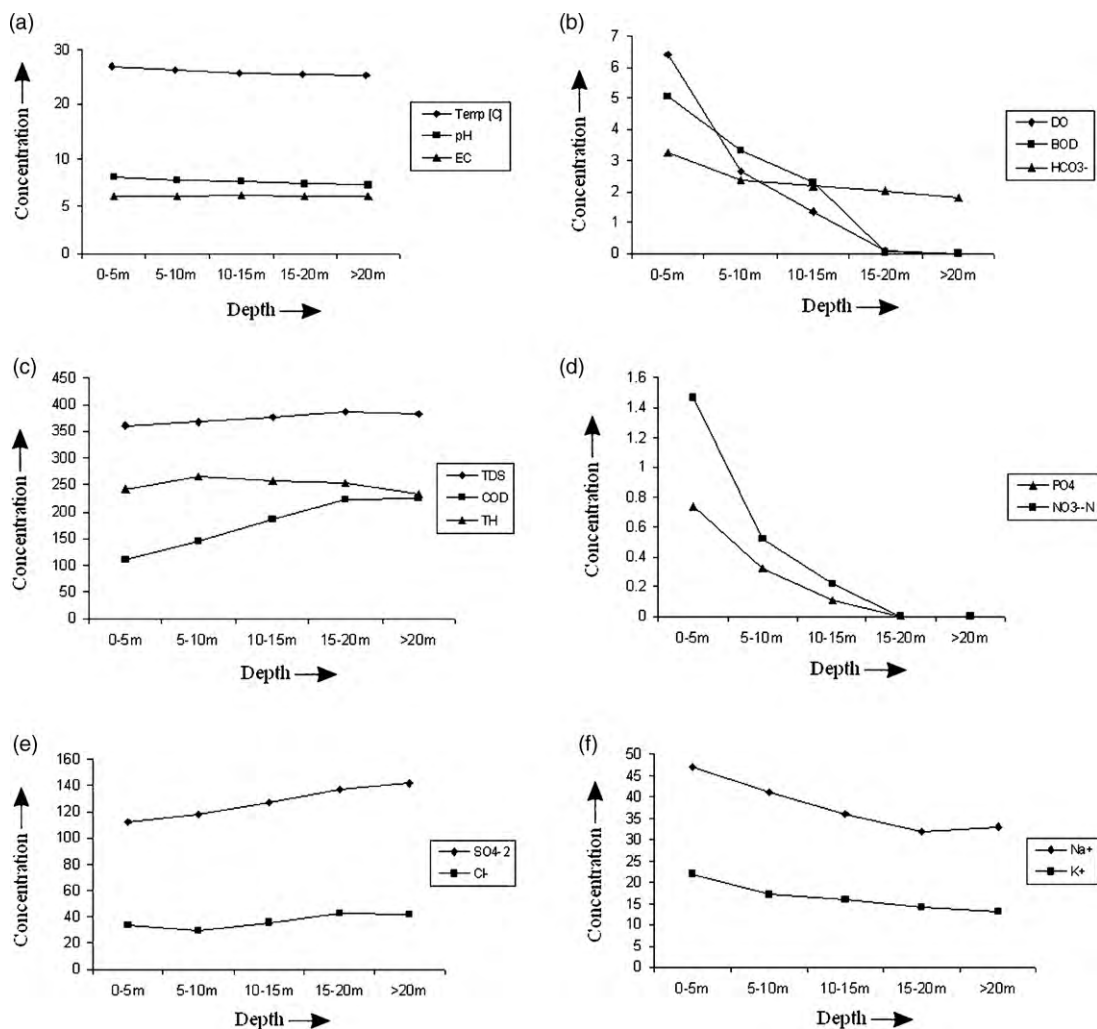[b] FAO irrigation standards [27].

Fig. 1. (a–f) Depth wise variations in limnological parameters of pit pond.

than those of the raw effluent as dilution plays an important role combined with the removal of pollutants by the natural processes [29].

3.2. Temporal changes and depth wise variation in the hydrochemistry of contaminated pit pond

3.2.1. Temporal changes

Among the studied water parameters (Table 2), temperature showed the most distinct temporal variations. Higher values of pH, TH, COD and other cations (Na^+, K^+) and anions (SO_4^{2-}, Cl^-) were noticed in summer, which can be explained by the high rate of evaporation during this season. Elevated DO content in monsoon may be explained by circulation and intermixing of atmospheric O_2 onto the surface layer, while considerable higher influx of surface runoff from adjoining land areas contributes significantly for higher EC, TDS, BOD, PO_4^{3-}-P and NO_3^--N content in OCP water. Decrease in pH, TH, COD, SO_4^{2-}, Cl^-, Na^+, K^+ during monsoon because of dilution of OCP water due to precipitation and surface runoff influx. DO content and COD value was lowest in winter, while TDS, BOD and HCO_3^- showed minimum/least value at summer season. Higher values of different limnological parameters during summer, and minimum values during monsoon were well documented by earlier workers [30,31]. This investigation showed the higher metal concentrations in OCP water during summer and lowest metal content in monsoon can be attributed to reduction in OCP water and dilu-

tion of OCP water in respective season, consistent with the earlier findings [32,33].

3.2.2. Depth wise variations

The depth wise investigation of pit pond hydrochemistry (Fig. 1(a–f)) revealed distinct three layer stratification – the surface oxic layer – epilimnion (0–5 m), an intermixing layer (5–8 m) separates the surface and sub-surface layer and a deeper sub-oxic/anoxic zone, where hypolimnion and monimilimnion merged into a single layer (8 to >25 m). Water pH and temperature decreases with increasing depth. Sharp decline in temperature, DO, BOD, NO_3^--N and PO_4^{3-}-P content was observed at depth of 5–8 m, can be explained by the intermixing of surface oxic layer with the sub-oxic deeper layer. After this zone, little change in temperature was observed. DO, BOD, NO_3^--N and PO_4^{3-}-P content decreased with increasing depth and become trace to undetectable at a depth of >15 m TDS, TH, COD, SO_4^{2-} and Cl^- showed increasing trend with the depth, while EC, HCO_3^-, Na^+, K^+, did not show any specific trend in their distribution. Metal content at different layer of OCP water (Table 4) showed positive relationship with increasing depth, and elevated metal concentrations in deeper layer can be explained by the anoxic conditions facilitates higher precipitation of metals collaborating with earlier investigations [8,9]. Although the, vertical trends of these parameters showed slight seasonal variations, but the general characteristics remain relatively constant throughout the year [10].

Table 3
Physico-chemical analysis of shallow sediments of contaminated pit pond.

Physical parameters	Contaminated pit pond	Uncontaminated pit pond		
pH	7.28 ± 0.18	7.12 ± 0.25		
EC (ms 25°C)	14.05 ± 2.59	11.08 ± 2.42		
CEC	118.25 ± 5.06	129.50 ± 6.14		
OM (%)	4.08 ± 0.43	4.98 ± 0.27		
Metal content (mg kg^{-1})	Contaminated pit pond	Uncontaminated pit pond	Reference value TEC [a]	Reference value PEC [b]
Fe	376 ± 24.60	106.50 ± 9.32	–	–
Cr	423 ± 30.57	122 ± 6.32	35.8	111
Cd	26 ± 4.69	14.5 ± 2.06	0.99	4.98
Pb	111 ± 4.97	53 ± 6.70	35.8	128
Mn	174 ± 8.52	110 ± 10.47	–	–
Zn	155 ± 7.62	102 ± 11.63	121	459
Cu	67 ± 5.29	34.5 ± 4.70	31.6	149

EC, ms at 25°C, CEC, meq g^{-1} of soil.
[a] TEC, Threshold Effect Concentrations [35].
[b] PEC, Probable Effect Concentrations [35].

Correlation study (r) among the different water parameters (excluding metals) revealed significant positive correlations ($p < 0.05$) between EC–HCO$_3$ (0.903), EC–K$^+$ (0.948), DO–BOD (0.918), DO–NO$_3^-$ (0.966), TDS–COD (0.916), TH–SO$_4^{2-}$ (0.928) and Cl$^-$–SO$_4^{2-}$ (0.982), which may be explained by similar pattern of distribution (irrespective of season and depth) due to their interdependence/influence on each other. DO content in pit pond water is negatively correlated ($p < 0.05$) with TDS (−0.945) and SO$_4^{2-}$ (−0.979), as DO decreases with increasing depth – opposite to TDS and SO$_4^{2-}$ showed elevated concentrations with depth.

3.3. Metal concentration and its fractions in OCP shallow sediments

Sediments generally possess high ability to absorb metals. Several sediment characteristics – pH, EC, redox potential, CEC and organic matter (OM) content are known to affect the accumulation, distribution, solubility and speciation of metals [14,34]. The pH of shallow OCP sediments is slightly alkaline with low organic matter load, while conductivity (EC) and cation exchange capacity (CEC) values are at moderate range. Metal content of shallow sediments of contaminated pit pond and uncontaminated pit pond are represented in Table 3. Metal abundance is in the sequence of Cr > Fe > Mn > Zn > Pb > Cu > Cd. The concentrations of Cr, Cd, Pb, Zn and Cu concentrations exceeded the TEC (Threshold Effect Concentrations), while Cr and Cd content were higher than recommended PEC (Probable Effect Concentrations) value [35]. The elevated concentrations of metals in shallow pit pond sediments can be attributed to effluents discharged by these surrounding industries thereby contaminating the superficial sediments.

Speciation study of metals provides much useful information regarding chemical nature and potential mobility of an element, which consequently can offer a more realistic estimate of actual environmental impact [34]. Results obtained from sequential extraction of shallow OCP sediments (Table 4) revealed that residual fractions were predominant for most of the metals, and metals were in their insoluble phases, strongly adsorbed onto the sediment particles. Redox metals (Fe, Mn and Cu) were fractionated as oxihydroxides (reducible) form can be explained by their higher potentiality to undergo oxidation/reduction reactions in aquous environment. Bioavailable-exchangeable fractions were much low, while least amount of metal fractions found to be organically bounded. Metal fractionation are in the order of residual fractions > Fe–Mn oxyhydroxides (reducible) > soluble-exchangeable > organically bounded and sulphides (oxidisable). Our investigation consistent with earlier workers [36], who also reported major metal fractions as residual and reducible fractions

with insignificant organic matter bounded fractions. The major metal fractions in reducible form can be explained due to the sub-oxic conditions in shallow OCP sediments which facilitate precipitation and adsorption of metals onto the sediments [37,38] which later becomes a part of matrix due to prolonged sedimentation process [39].

3.4. Factor analysis (PCA extraction) for contaminated OCP water and shallow sediments

Factor analysis (PCA extraction) of metal contents in OCP water and sediments were used as a statistical mean to identify different pollution sources. Factor analysis of OCP water (Table 5) concluded three factors (eigen value >1) considering 78.18% of total variance in data set. F1 explained for EC, TDS, BOD, HCO$_3^-$, PO$_4^{3-}$, NO$_3^-$, SO$_4^{2-}$, Cl$^-$, Cr, Zn, and attributed to surface runoff inputs and background lithogenic factors. F2 explained for pH, COD, Fe, Cd, Pb, Mn, Cu, which can be correspond with the anthropogenic influence – i.e. discharge of industrial effluents in the studied pit pond while F3 – explained for Temperature, DO, TH may be related with natural physico-chemical factors (temporal changes and precipitation).

Factor loading in OCP shallow sediments (Table 5) considered two factor (eigen value >1) covering 82.24% of total variance in total data set. F1 explained for EC, Fe, Cd, Pb, Mn, Cu, and can be attributed

Table 4
Distribution of metals in water column and metal fractionations in shallow sediments of contaminated pit pond.

	0–5 m	5–10 m	10–15 m	15–20 m	>25 m
Metal distribution in different compartment of OCP water					
Fe	0.148	0.166	0.184	0.223	0.228
Cr	0.766	0.776	0.784	0.794	0.790
Cd	0.007	0.006	0.006	0.005	0.005
Pb	0.022	0.024	0.026	0.029	0.030
Mn	0.380	0.394	0.412	0.427	0.434
Zn	0.216	0.227	0.230	0.224	0.237
Cu	0.144	0.153	0.166	0.164	0.169

	Residual	Reducible	Oxidisable	OM bounded	Total
Metal fractions in shallow OCP sediments					
Fe	136	172	52	16	376
Cr	184	153	64	22	423
Cd	11	8	5	2	26
Pb	51	34	18	8	111
Mn	60.5	72	29	12.5	174
Zn	66	43	31	14	154
Cu	22	30	8	6	67

Metal content, mg kg^{-1}.

Table 5
Factor analysis (PCA extracting) for OCP water and sediments.

	F1	F2	F3
Pit pond water			
Temp ($^\circ$C)	0.473	−0.0391	**0.789**
pH	0.461	**0.600**	−0.027
EC	**0.712**	−0.057	0.302
TDS	**0.631**	0.425	0.398
DO	0.324	−0.490	**−0.704**
BOD	**0.520**	0.339	−0.175
COD	0.360	**0.736**	−0.504
TH	0.324	−0.131	**0.524**
HCO_3^-	**0.599**	−0.324	0.105
PO_4^{3-}-P	**−0.720**	−0.038	0.324
NO_3^--N	**0.903**	0.063	−0.124
SO_4^{2-}	**0.692**	0.325	−0.554
Cl^-	**0.681**	0.265	−0.090
Na^+	**0.730**	−0.016	0.395
K^+	**0.682**	−0.041	0.597
Fe	0.329	**0.798**	−0.116
Cr	**0.667**	0.543	0.209
Cd	0.329	**0.860**	−0.023
Pb	0.435	**0.675**	−0.017
Mn	0.377	**0.673**	0.206
Zn	**0.769**	0.585	0.210
Cu	0.432	**0.726**	−0.029
Eigen value	10.785	6.435	4.800
Variability	48.930	29.252	21.818
Cumulative	48.930	78.182	100.00

	F1	F2
Pit pond sediments		
pH	0.201	**−0.966**
EC	**−0.640**	0.062
OM	0.489	**0.688**
CEC	0.453	**0.752**
Fe	**0.996**	0.033
Cr	0.426	**−0.870**
Cd	**0.993**	0.033
Pb	**0.974**	0.079
Mn	**0.997**	0.061
Zn	0.221	**−0.824**
Cu	**0.988**	−0.088
Eigen value	8.770	1.223
Variability	79.729	11.114
Cumulative	79.729	90.843

Values in bold indicates significant loading.

to the metal enrichment in OCP water due to industrial discharge. F2 explained for pH, OM, CEC, Cr, Zn can be corresponded with the geogenic factors. Some of the metals viz Fe, Cr, Zn showed noticeably higher loading for more than one factor may be explained by their combined-multiple sources (anthropogeic influence, geological processes or background lithogenic factor).

Regression analysis between metal concentrations in pit pond water with shallow sediment metal content revealed significant ($p < 0.05$). R^2 values for Fe (0.973), Cr (0.970), Pb (0.949) and Mn (0.940), which can be explained by the elevated concentrations of these metals in contaminated pit pond water that

results subsequent precipitation and adsorption of these metals on sediments. Besides, sediment characteristics and prevailing environmental/geological conditions also might be the governing factor for the accumulation of metals.

3.5. Assessment of metal contamination in OCP water and sediments

Several studies [26,34,39,40,41] demonstrated that the concentrations of metals in water and sediments can be sensitive indicator of contaminants in hydrological system. Elevated concentrations of metals in water and sediments are often related with toxic effects on aquatic ecosystem. Contamination index (C_d), geoaccumulation index (I_{geo}), pollution load index (PLI) and heavy metal evaluation index (HEI) were successfully used by earlier workers singly or in combination for assessment of metal enrichment/contamination in water–sediments. Contamination index (C_d) is used to evaluate the degree of contamination of water and represents the combine effects of several quality parameters considered as harmful. On the basis of contamination level, C_d values are categorized as low ($C_d < 1$), medium ($C_d = 1$–3) and high ($C_d > 3$) [22]. Geoaccumulation index (I_{geo}) originally proposed for a quantitative measure of the metal pollution in aquatic sediments. Geoaccumulation index classified as I_{geo} value >0–1 = uncontaminated to moderate, >1–2 = moderate, >2–3 = moderate to strong and >3–4 = strong or highly polluted [23]. Pollution load index (PLI) provides a simple, comparative means for assessing soil-sediment quality. PLI = 0 indicated perfection or control, PLI value of 1 represented the baseline level of pollutants while PLI > 1 indicated progressive deterioration of site due to elevated metal content [42]. Heavy metal index (HEI) provides an overall quality of water–sediments in relation with metal enrichment due to natural and anthropogenic influences [25].

In this present investigation, all these indices have been used to represent an integrated picture of metal contamination of pit pond due to industrial discharge and are presented in Table 6. The high C_f value for Cr, Mn, Cu and Cd in contaminated OCP water and C_d value of all the sampling sites indicated the high (>3). The high contamination of OCP water can be attributed to direct discharge of industrial effluents into the pit pond. The geoaccumulation of metals in shallow OCP sediments is in the sequence of Fe > Cr > Pb > Cu > Cd > Mn > Zn. The correlations study between metal C_f of OCP water and I_{geo} value of metal did not show any significant interrelations, but strong positive correlations ($p < 0.05$) were found C_f with I_{geo} value for Fe, Cr, Pb, Cu and Mn in OCP sediments. The elevated C_f value of the studied metals can be corresponded with higher precipitation of metals and their subsequent geoaccumulation in shallow OCP sediments (Table 6). The pollution load (PLI) for shallow sediments was moderate to high, and the heavy metal evaluation index (HEI) of both water and shallow sediments were in moderate range. Moderate contamination of shallow OCP sediments can be explained by less geoaccumulation of metals due to the prevailing sub-oxic condition.

Table 6
Metal contamination in water and sediments of pit pond with contamination index (C_d), pollution load index (PLI) and Heavy metal evaluation index (HEI).

Metals		Fe	Cr	Cd	Pb	Mn	Zn	Cu
OCP water	C_f	0.03	7.62	0.7	0.004	1.9	0.108	0.72
	Contamination index (C_d) = 7.52							
	Heavy metal evaluation index (HEI) = 11.08							
OCP sediments	C_f	3.52	3.47	1.81	2.09	1.58	1.52	1.94
	I_{geo}	1.23[*]	1.21[*]	0.27	0.47[*]	0.074[*]	0.019	0.36[*]
	Pollution load index (PLI) = 2.272							
	Heavy metal evaluation index (HEI) = 15.91							

C_f, contamination factor; I_{geo}, index of geoaccumulation.
[*] $p < 0.05$.

4. Conclusion

There were certain changes observed in the hydrochemistry of contaminated pit pond water and industrial effluents discharge have been identified as major pollutant sources; but the major attention gained by metal distribution in shallow sediments and overlying water column. The problem was not so severe with metal contamination in OCP water and can be used for agricultural applications, but the geoaccumulation of metals in OCP sediments can be an environmental concern in long run due to distribution and exchange of metals in sediment–water interface. The concentration and speciation of metals in water and sediments may vary depending upon the oxic-anoxic conditions and also temporal variations. Therefore detail investigations on metal distribution in different layer/compartment of OCP water as well as numerical evaluation of metal accumulation rate in bottom sediments of pit pond can be more useful for better toxicological assessment of contamination at water–sediment system.

Acknowledgements

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