Environ Earth Sci (2012) 67:2053–2061
DOI 10.1007/s12665-012-1644-9

ORIGINAL ARTICLE

Major ion chemistry and metal distribution in coal mine pit lake contaminated with industrial effluents: constraints of weathering and anthropogenic inputs

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Received: 18 July 2011 / Accepted: 14 March 2012 / Published online: 28 March 2012

Abstract Ion chemistry of mine pit lake water reveals dominance of alkaline earths (Ca^{2+} and Mg^{2+}) over total cation strength, while SO_4^{2-} and Cl^- constitute the majority of total anion load. Higher value of $Ca^{2+} + Mg^{2+}/Na^+ + K^+$ (pre-monsoon 5.986, monsoon 8.866, post-monsoon 7.09) and $Ca^{2+} + Mg^{2+}/HCO_3^- + SO_4^2$ (pre-monsoon 7.14, monsoon 9.57, post-monsoon 8.29) is explained by weathering of Ca–Mg silicates and dissolution of Ca^{2+}-bearing minerals present in parent rocks and overburden materials. Silicate weathering supposed to be the major geological contributor, in contrast to bicarbonate weathering does a little. Distribution coefficient for dissolved metals and sorbed to surface sediments is in the order of Cd > Pb > Fe > Zn > Cu > Cr > Mn. Speciation study of monitored metals in surface sediments shows that Fe and Mn are dominantly fractionated in exchangeable-acid reducible form, whereas rest of the metals (Cr, Pb, Cd, Zn, and Cu) mostly in residual form. Cd, Pb, and Zn show relatively higher recalcitrant factor that indicates their higher retention in lake sediments. Factor loading of monitored physico-chemical parameters resembles contribution/influences from geological weathering, anthropogenic inputs as well as natural temporal factors. Ionic load/strength of lake water accounted for geochemical process and natural factors, while pollutant load (viz BOD, COD and metals, etc.) is associated with anthropogenic inputs through industrial discharge.

Keywords Ion chemistry · Distribution coefficient (K_d) · Metal speciation · Factor analysis

Introduction

Lakes generally posses definite clear cut boundary, and represent one of the most versatile ecosystem on the earth. A major fraction of dissolved ions, heavy and trace metals are supposed to be contributed by geological weathering and lithogenic sources. The concentration of chemical constituents depends on the availability of the parent material for a particular constituents and its dissolving capacity (Jeelani and Shah 2006). Climatic influence/impacts on chemical weathering might also be the reasons for the differences in the thermodynamic and kinematics interactions between minerals and solutions (Das and Kaur 2001; Anshumali and Ramanathan 2007). The weathering of catchment's rocks, the disintegration of and decay of their constituent minerals liberate elemental ions and act as a natural source of pollution; however, human actions often cause pollution of much greater magnitude than natural contributions in lake systems (Das 2005; Das and Kaur 2001). Due to drastic rise in urban and industrial developments in the lake surroundings made them vulnerable to problems, such as pollution, rapid sedimentation and high mobilization rates, etc., the lake water quality decreasing throughout the world has become a direct threat to many life forms (Sujatha et al. 2001; Chakrapani 2002). Lentic water bodies are the main victims of pollution, because the dispersion rate of pollutants/waste matter is very low and mobilization rate is high. Large quantities of metals are being released into the environment (i.e. air, water, soil) from mining, industrial agricultural and other anthropogenic waste due to inadequacies of technology in the processing of metals. Characteristics of mine pit lake water can vary

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greatly (with season and depth) in the concentrations of contaminants present and can be a potential water resource to fulfill the local water demands for industrial, irrigation, and other uses (Cidu and Biddau 2007; Gupta et al. 2010).

Present investigation aiming to illustrate the hydrochemistry and anthropogenic influence on mine pit lake contaminated with industrial discharge in the light of (1) major ion chemistry of pit lake water, (2) metal partitioning coefficient in water sediments, (3) metal speciation and retention in lake surface sediments.

Regional geology and geomorphology of Raniganj coal field area

Raniganj coal field lies in the easternmost part of the Damodar valley coal field area, covers about 1,530 km^2 of area of Burdwan, Birbhum, Bankura, Purulia district of West Bengal and Dhanbad district in Jharkhand. The geographical topography of this area is gently undulating and the elevation generally ranges from 60 to 75 m above the sea level. This region under tropical climatic conditions has wide variations in temperature (min 4–5 °C in winter to max 42–44 °C in summer) with average annual rainfall of 1,250 mm. This coal field area is also the oldest coal mining area in India (started since 1774) containing bituminous and sub-bituminous coal, and possesses both underground as well as open cast coal mining by Eastern coal India Ltd. This coalfield belongs to the lower Gondwana Raniganj formation (Upper Permian), mostly surrounded by Archean rocks (granites, granitic gneiss) except in east, and consists of a repetitive sequence of sandstone, shale, carbonaceous shale and extensive coal seams. Geological succession of Raniganj Coal field area has been stated in the previous investigation (Singh et al. 2010) presented in Table 1.

The field study was conducted at Mangalpur (latitude 23°37′N and longitude 87°08′E), a well-known industrial complex in eastern Raniganj coal field area, situated in western part of the state West Bengal, India and had open cast coal mining in the past (Fig. 1). After end of mining, open cast coal pits were filled up with precipitation and ground water influx and converted into pit pond. This industrial complex is in the status of a developing industrial estate comprising altogether six 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 open cast pit pond (OCP) having surface area of about 64,000 m^2. Previous investigation shows effluents released by these industries are alkaline in nature with high dissolved solids which exceeds the prescribed Indian Standards (IS: 2490 Part 1, 1981 for effluents discharge into surface waters). Total hardness and COD value are also high but within IS standards, and low BOD value indicates lesser amounts of biodegradable pollutant load. Effluents are poor in nutrient content, while SO_4^{2-} and Cl^- content are in moderate range. Among studied metals, Fe and Pb contents are higher than IS discharge standards and other metals are within permissible limits (Gupta et al. 2010). Noticeable metal translocation also reported along vertical and lateral distance from effluents discharge channel (Nayek et al. 2011).

Methodology

Sample collection and analytical processes

Periodical sampling of contaminated OCP water was carried out on a duration from 2008 to 2010, covering all seasons. Representative pit pond water samples were collected in 1 L wide mouth plastic bottles, pre-washed with double-distilled water. Before sampling, bottles were

Table 1 Geological succession of Raniganj coal field area

Geological age	Formation	Major lithology
Recent	River alluvium unconformity	Sand, clay, and limestones
Jurassic to Cretaceous	Rajmahal trap or intratrappeans	Dolerite, mica peridotite dykes and sills
Upper Triassic	Supra Panchet unconformity	Sand stone and shale
Lower Triassic	Panchet series	Medium to coarse grained feldspathic sand stone and red clays
Upper Permian	Raniganj measures	Fine to medium grained sand stone, sandy/micaceous shale, coal seams, silt stone and carbonaceous shale
Middle Permian	Iron stone shale	Carbonaceous shale containing nodules of clays
Lower Permian	Barakar measures	Massive sand stones and grits with shale beds and coal seams
Upper carboniferous	Talchir series unconformity	Tillites to boulder conglomerate, yellowish green sand stone, etc.
Archaen	Metamorphic rocks with igneous intrusive	Granites, granitic gneiss, hornblende schist, pegmatite and veins of quartz

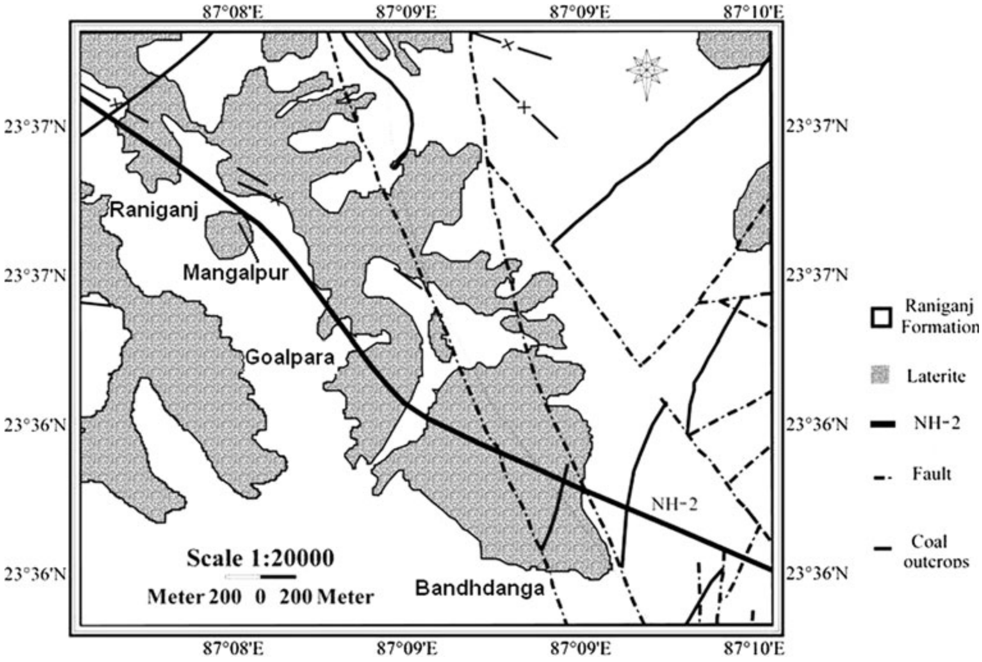

Fig. 1 Geological disposition of Mangalpur and surrounding area

rinsed with sample water. Temperature, pH, EC and TDS were measured in the field using a water thermometer and portable hand analyzer (Hannah; HI 98121). Collected water samples were filtered through Whatman's 42 and refrigerated under 4 °C in laboratory for further physico-chemical analysis. Major cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and anions (SO_4^{2-}, Cl^{-}, NO_3^{-}, and PO_4^{3-}), dissolved silica (Si) were measured following the standard methods (APHA 1998).

For determination of metal concentrations (Fe, Cr, Cd, Pb, Mn, Cu, and Zn) in pit lake water, 1-L water samples are digested with 70 % HNO_3 acid in microwave (600 W, for 6 min), filtered with GFC and diluted to 50 ml with distilled water, and then analyzed in atomic adsorption spectrophotometer (AAS) (GBC, avanta). Pit lake sediment samples were collected from six different sites throughout the season. Shallow surface sediments samples were collected using stainless steel dagger to avoid further metal contamination, and kept in plastic zipped bags. Samples were air dried, sieved (2 mm) and digested with (3:1) HNO_3 and $HClO_4$ in microwave in 600 W, for 10 min. Digested samples were diluted to 50 ml with distilled water, and for analysis for total metal content in AAS (GBC, avanta).

Chemical speciation/fractionation of metals was determined by sequential extraction procedure as per BCR (Community Bureau of Reference) optimized three-step sequential extraction procedure (modified by Rauret et al. 1999).

(1) Exchangeable metals: 1.00 g of dry soil sample extracted with 40 ml of 0.11 mol L^{-1} acetic acid. The mixture was shaken for 12 h at room temperature and then extract was separated by centrifugation, (2) reducible metals: repeatedly washed residue was treated with 40 mL of 0.5 mol L^{-1} hydroxylamine hydrochloride (adjusted to pH 2 with HNO_3). After 12-h shaking at room temperature the mixture was centrifuged for 15 min, and then decanted. The residue was washed with distilled water, centrifuged, and the supernatant discarded, (3) oxidizable metals: residue was digested with 10 ml of 30% (w/v) H_2O_2 at room temperature for 1 h with occasional manual shaking. The solution was heated to near dryness, and 50 mL of 1.0 mol L^{-1} ammonium acetate solution (adjusted to pH 2 with nitric acid) was added to the moist residue. The sample solution was shaken and centrifuged, and the extract was separated, (4) residual metals: for metals insoluble in the previous steps, 6 mL of double-distilled water and then aqua regia (1:3 v/v of conc. $HNO_3 + HCl$) solution of 15 mL were added to the remaining residue. This residue was then digested in microwave. Digested solution was filtered by GF/C filter paper and volume makes up to 50 ml. The concentrations of Cd, Cr, Fe, Mn, and Pb in different sequential extract were measured in AAS (GBC, Avanta).

Statistical analysis and quality control

Factor analysis is a numerical method used here to describe how the geochemical processes influence the responses on a number of measured variables. Factor loading (PCA extraction with varimax rotation) of water parameters of pit lake is performed to analyze the variations of measured variables, and to identify possible origin by considering minimum eigenvalue >1. Measures that are highly correlated (either positively or negatively) are likely influenced by the same factors, while those that are relatively uncorrelated are likely influenced by different factors.

Linear regression analysis was performed between dissolved metals with different metal fractions in shallow sediments. All statistical analyses were performed at 0.05 and 0.01 % significance level.

E-Mark standard (AR grade) solution was used for calibration and preparation of standard curve. The analytical precision was maintained by triplicate each sample, and overall relative standard deviations were within ±2 % for all the parameters.

Results and discussion

Hydro-chemical assessment of pit lake water

The chemistry of lake water and sediment is a cumulative reflection of catchment's geology, weathering and erosional processes as well as anthropogenic inputs (Jeelani and Shah 2006). The higher values for EC and TDS in OCP water reveal its ionic strength/concentrations. In case of surface waters, the source of major ions can be identified by plotting variations in TDS with Na/Na + Ca as a function of weight rations (Gibbs 1970). Present investigation (Fig. 2) shows that rock weathering as major process for liberating ions in the lake basin and also responsible for controlling water chemistry along with contribution from anthropogenic sources (i.e. industrial effluents discharge).

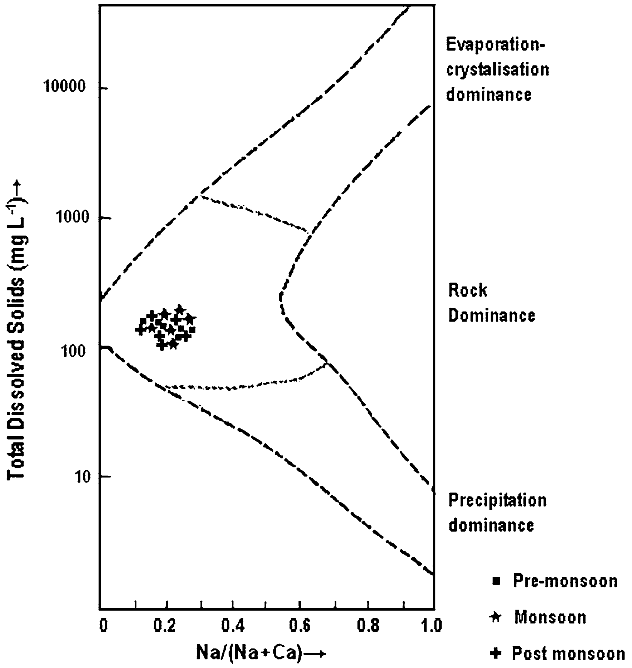

Fig. 2 Gibbs diagram (weight rations of TDS with Na/(Na + Ca)

The cation chemistry of OCP water (Table 2) is dominated by Ca^{2+} and Mg^{2+} followed by Na^+ and K^+ comprising 89.806–85.656 and 14.344–10.194 % of total cation balance in their equivalent weight. Ca^{2+} and Mg^{2+} are the common constituents of natural water and their higher value in open cast pit lake water in Raniganj formation areas was reported by Singh et al. (2010). Ternary cation diagrams of dissolved Si ($Na^+ + K^+$) and alkaline earths ($Ca^{2+} + Mg^{2+}$) are used as an index of weathering for igneous and metamorphic terrain (Singh and Hasnain 1999). The cationic plots are towards $Ca^{2+} + Mg^{2+}$ apex (Fig. 3) representing significant contribution by alkaline earths maintaining the cationic balance of pit pond water. The anion chemistry of pit lake water (Table 2) shows that SO_4^{2-} and Cl^- as dominated anions and in equivalent unit representing 77.388–75.443 % of total anion balance, followed by SiO_4^{2-} (21.818–19.788 %) and HCO_3^- (2.435–1.904 %). The relationship between chemistry and geology can also be evaluated by ternary anion diagrams relating dissolved Si, HCO_3^-, and $SO_4^{2-} + Cl^-$ (Stallard and Edmond 1983). The plotted points in the ternary anion diagram (Fig. 4) for pit lake water cluster are towards the $SO_4^{2-} + Cl^-$ apex with minor contribution from HCO_3^- (Fig. 4).

Geochemical weathering

Higher value of $Ca^{2+} + Mg^{2+}/Na^+ + K^+$ (>1) in all the seasons (Table 1) can be corresponded with weathering of Ca–Mg silicates chiefly from Ca—plagiodese, amphiboles, pyroxenes abiotite present in parent rocks and overburden materials. The low value of $HCO_3^-/Ca^{2+} + Na^{2+}$ for all the seasons (<1) supports minor contribution from carbonate weathering. Ca^{2+}/SO_4^{2-} ratio (>1) indicates that H_2SO_4 does not replace H_2CO_3 as source of protons required for rock weathering (Stallard and Edmond 1983). The $Ca^{2+} + Mg^{2+}/Tz^+$ ratio (Table 2) reflects the abundance of Ca^{2+} and Mg^{2+} in pit lake water attributed to silicate weathering, consistent with lithology of the surrounding area. $Na^+ + K^+/Tz^+$ in different seasons infer that the contribution of cations from alumino-silicate weathering is low in comparison to (Ca, Mg) silicates weathering.

High Ca^{2+}/SO_4^{2-} ratio (>1) and low $HCO_3^-/HCO_3^- + SO_4^{2-}$ ratio (Table 1) indicate oxidative weathering of minerals such as pyrite (FeS_2), gypsum ($CaSO_4$), and andrite ($CaSO_4$) that occur in sandstone and shale overlying the coal seams and excavated overburden materials (Zhang et al. 1995; Singh and Hasnain 1999). However, mineral pyrite (FeS_2) is reported to occur as secondary mineral in these coals and associated sediments (Chandra 1992). The observed high values of SO_4^{2-} in pit pond water of the study area are

Table 2 Hydrochemistry of contaminated mine pit lake

Parameter	Pre-monsoon	Monsoon	Post-monsoon
pH	8.05 ± 0.076	7.68 ± 0.064	7.88 ± 0.048
EC (ms cm^{-1})	4.99 ± 0.513	7.64 ± 0.384	6.48 ± 0.469
TDS (mg L^{-1})	297.67 ± 16.693	359.83 ± 16.497	331.33 ± 8.919
Na^+ (mg L^{-1})	51.90 ± 4.221	31.98 ± 3.586	41.997 ± 3.993
K^+ (mg L^{-1})	18.53 ± 2.869	8.23 ± 0.747	15.01 ± 2.667
Ca^{2+} (mg L^{-1})	137.17 ± 5.811	114.17 ± 5.047	130.5 ± 3.452
Mg^{2+} (mg L^{-1})	115.00 ± 7.014	101.83 ± 3.933	109.33 ± 3.94
HCO_3^- (mg L^{-1})	6.30 ± 0.569	3.82 ± 0.245	4.18 ± 0.414
SO_4^{2-} (mg L^{-1})	105.60 ± 11.087	68.24 ± 6.815	86.85 ± 5.836
Cl^- (mg L^{-1})	38.59 ± 2.707	27.56 ± 3.039	32.76 ± 2.483
NO_3^- (mg L^{-1})	0.898 ± 0.058	1.35 ± 0.064	0.68 ± 0.060
PO_4^{3-} (mg L^{-1})	0.063 ± 0.008	0.081 ± 0.005	0.059 ± 0.005
SiO_4^- (mg L^{-1})	38.69 ± 3.388	28.98 ± 3.670	36.23 ± 2.864
$Ca^{2+} + Mg^{2+}/Na^+ + K^+$	5.99 ± 0.36	8.87 ± 0.803	7.09 ± 0.872
$Ca^{2+} + Mg^{2+}/HCO_3^- + SO_4^{2-}$	7.14 ± 0.821	9.57 ± 1.150	8.29 ± 0.623
$HCO_3^-C/a^{2+} + Na^+$	0.006 ± 0.001	0.004 ± 0.00	0.004 ± 0.00
$HCO_3^-/Ca^{2+} + Mg^{2+}$	0.006 ± 0.001	0.004 ± 0.000	0.004 ± 0.000
$SiO_4^-/Na^+ + K^+$	0.31 ± 0.011	0.40 ± 0.082	0.36 ± 0.044
$SiO_4^-/Ca^{2+} + Mg^{2+}$	0.052 ± 0.005	0.045 ± 0.006	0.051 ± 0.005
Ca^{2+}/SO_4^{2-}	3.14 ± 0.372	4.05 ± 0.524	3.62 ± 0.301
Ca^{2+}/Na^+	3.05 ± 0.23	4.14 ± 0.48	3.6 ± 0.44
$SO_4^{2-} + Cl^-/HCO_3^-$	31.96 ± 2.842	35.21 ± 2.954	40.24 ± 4.036
$HCO_3^-/HCO_3^- + SO_4^{2-}$	0.045 ± 0.004	0.043 ± 0.006	0.037 ± 0.004
$Ca^{2+} + Mg^{2+}/Tz^+$	0.857 ± 0.007	0.898 ± 0.009	0.875 ± 0.014
$Na^+ + K^+/Tz^+$	0.143 ± 0.007	0.102 ± 0.009	0.125 ± 0.014

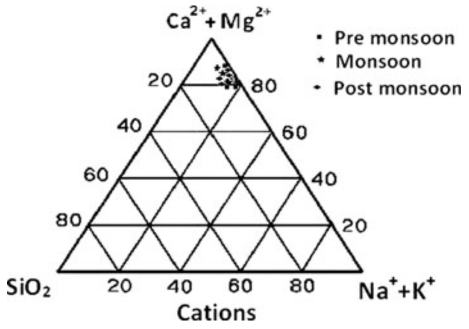

Fig. 3 Trilinear diagram for cations

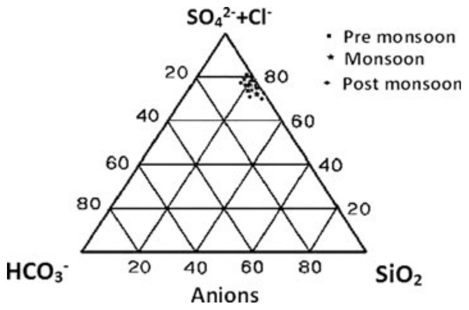

Fig. 4 Trilinear diagram for anions

attributed to the weathering of pyrites by the following reactions (Lowson et al. 1993)

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

Silica concentrations may reflect some silicate mineral weathering in the lake's catchments. The silica concentration notably higher in all the seasons indicates that silica minerals within the rock-bearing minerals are susceptible to weathering condition. The overall high pH throughout the season also supports the high rate of silicate weathering. The general reactions for weathering of silicate minerals with H_2CO_3 can be written as

$$(Na, K, Mg, Ca)\ Silicate + H_2CO_3 \leftrightarrow H_4SiO_4 + HCO_3 + Na + K + Mg + Ca + solid\ product.$$

In general, pit pond water in the Raniganj formation is characterized by higher concentrations of Na^+, HCO_3^-, dissolved silica and high Na^+/Cl^- and $Na^+ + K^+/Tz^+$ ratio (Singh et al. 2010), but the studied pit lake water, in spite of its occurrence in the Raniganj formation is dictated by the inputs of untreated effluents from sponge iron industries. Predominance of Ca^{2+} and Mg^{2+} over Na^{+} and K^{+} partly responsible for the weathering of Ca–Mg silicates and crystalline dolomitic limestones occurs as isolated bands in the study area, in collaboration with earlier findings (Singh and Hasnain 1999; Singh et al. 2008).

Anthropogenic contribution/influence

Many studies reveal that variation in TDS in groundwater may be related to land use and also to pollution (Han and Liu 2004; Jalali 2009). The source of Cl^{-}, SO_4^{2-}, and NO_3^{-} ions is mostly agricultural fertilizers, animal wastes and industrial and municipal sewage, and correlation of these ions with TDS can be used to indicate the influence of human activities on the water chemistry (Han and Liu 2004; Jalali 2009). Increase in Ca^{2+} and Mg^{2+} concentrations with increasing TDS supports the anthropogenic input mainly domestic and industrial wastes (Singh et al. 2010). Noticeable contribution of Ca^{2+} and Mg^{2+} may occur from the dissolution of overburden materials, and effluents from sponge iron industries use dolomitic limestones as major ingredients for processing sponge iron.

SO_4^{2-} and Cl^{-} concentrations in pit lake water exhibit positive trend with increasing TDS, indicating same source and can be used as pollution indicators for anthropogenic input (Choi et al. 2005; Jalali 2009). In the study area, strong positive correlations have been observed between TDS with SO_4^{2-} and Cl^{-} ($r = 0.821$ and 0.792, respectively) suggesting common source mainly anthropogenic activities. A positive correlation ($r = 0.724$) between TDS with $(SO_4^{2-} + Cl^{-})/HCO_3^{-}$ and molar ratio >1 (2.03) supports the anthropogenic inputs. In addition to the geochemical weathering, the possible source of SO_4^{2-} and Cl^{-} in study area is mainly industrial effluents and domestic sewage (Gupta et al. 2010).

Results indicate influence of complex contamination sources and geochemical process. Dominance of weak acids (HCO_3^{-}) over strong acids (SO_4^{2-} and Cl^{-}) is common characteristics for majority of pit lake water, but the studied pit pond shows the reverse situation. Higher concentrations of TDS, SO_4^{2-}, and Cl^{-} suggest the impact of anthropogenic influences (by means of industrial effluents discharge) on water chemistry of examined pit lake.

These phenomena are also supported by statistical analysis, where dominance of several factors is noticed. Factor analysis (PCA extraction) for physico-chemical parameters of pit lake water (Table 3) considered three factors (eigenvalue >1) covering 74.32 % of total variance of given data set. F1 shows higher loading for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, NO_3^{-}, SO_4^{2-}, and $HSiO_4^{3-}$, explained by geogenic/lithogenic contribution as well as surface runoff. Factor 2 explained for pH, TDS, BOD, COD, PO_4^{3-}, Cl^{-} which can be attributed to anthropogenic sources, whereas F3 explained for temperature, EC and DO can be corresponded with seasonal/other natural factor. Some of the parameters, viz SO_4^{2-}, Cl^{-} exhibit noticeable higher loading for more than one factor, which may be due to their multiple origin/sources.

Table 3 Factor analysis (PCA extraction) of pit lake water

	F1	F2	F3
Temp (°C)	0.473	−0.391	0.789
pH	−0.281	−0.752	0.597
EC	0.441	0.165	0.882
TDS	0.425	0.813	0.398
DO	0.217	0.613	−0.760
BOD	0.495	−0.830	−0.257
COD	0.495	−0.859	0.132
Ca^{2+}	0.985	0.067	−0.160
Mg^{2+}	0.863	0.306	0.127
Na^{+}	−0.819	−0.285	0.498
K^{+}	0.674	0.283	−0.683
HCO_3^{-}	0.859	−0.423	0.288
PO_4^{-3}	0.389	0.790	0.473
$NO_3^{-}N$	0.901	0.380	0.208
SO_4^{-2}	−0.680	−0.616	−0.397
Cl^{-}	0.554	−0.810	−0.193
$HSiO_4$	0.934	0.047	−0.362
Fe	−0.045	0.977	−0.207
Cr	0.059	0.743	−0.667
Cd	−0.255	0.949	−0.186
Pb	0.053	0.990	−0.132
Mn	0.015	0.994	0.027
Zn	0.137	0.984	−0.114
Cu	0.221	0.900	0.375
Eigenvalue	10.553	3.873	3.302
Variability	47.968	17.603	15.007
Cumulative	47.968	65.572	86.191

Metal concentrations and partitioning in water sediments of pit lake

Concentrations of heavy and trace metals are an indication of the extent of pollution in an aquatic environment. Dissolved metal concentrations in pit lake water and total metal content in shallow sediments are given in Table 4, and the magnitude of metal content is noticeably higher than desirable standards or control/background value for surface water and sediments. Results of this study very much resembles the previous investigation (Gupta et al. 2010), who also reported the same. Trace element

Table 4 Metal concentrations in pit lake water and shallow sediments, with metal partitioning (log K_d)

Metals	Dissolved metal (mg L^{-1}) (max–min ± SD)	Sediment metal content (mg kg^{-1}) (max–min ± SD)	log K_d (max–min ± SD)	Regression analysis (linear)
Fe	0.152 − 0.118 ± 0.013	439.60 − 317.60 ± 50.08	3.461 − 3.430 ± 0.013	$y = 34.88x - 1{,}345$, $R^2 = 0.986$
Cr	0.80 − 0.555 ± 0.098	489.40 − 359.40 ± 52.29	2.834 − 2.757 ± 0.030	$y = 21.24x - 885.3$, $R^2 = 0.987$
Cd	0.007 − 0.004 ± 0.001	27.50 − 24.10 ± 1.33	3.780 − 3.594 ± 0.072	$y = 3.998x - 220.9$, $R^2 = 0.952$
Pb	0.025 − 0.020 ± 0.002	119.50 − 101.50 ± 7.28	3.705 − 3.679 ± 0.011	$y = 3.519x - 187.0$, $R^2 = 0.929$
Mn	0.393 − 0.295 ± 0.039	192.80 − 154.80 ± 15.17	2.736 − 2.674 ± 0.024	$y = 2.800x - 66.35$, $R^2 = 0.988$
Zn	0.230 − 0.146 ± 0.036	164.00 − 141.00 ± 9.02	2.993 − 2.839 ± 0.079	$y = 11.12x - 641.9$, $R^2 = 0.943$
Cu	0.156 − 0.090 ± 0.026	71.60 − 63.80 ± 3.07	2.851 − 2.653 ± 0.096	$y = 0.674x - 10.19$, $R^2 = 0.974$

* $P < 0.05$; ** $P < 0.001$

concentrations in lakes are mainly governed by exchanges between sediment and water processes in the lake catchments, in the water column and processes at the sediment surface (Chakrapani 2002).

Geochemical investigation requires the detail understanding of interaction of metals in solid–solution phases. K_d is important for the evaluation of potential adsorption of dissolved contaminants in contact with sediment/soil surface (Knox et al. 2006). Partitioning coefficient (K_d) of dissolved metals in pit lake water and adsorbed to shallow sediments of pit lake is calculated as

$$\mathbf{K_d} = \frac{\text{Metal concentration in solid phase (mg/Kg)}}{\text{Metal concentration in dissolved phase (mg/L)}}.$$

Log K_d value for dissolved metals with sorbed metals in shallow sediments is given in Table 4. The relatively higher K_d values (log $K_d > 3.3$) observed for Pb, Cd, and Fe indicate their preferential association and enrichment in sediments. Relatively lower K_d values for Mn, Zn, Cr, and Cu indicate that they are less likely to be associated with sediments.

Speciation of metals and their retention in shallow pit lake sediments

Speciation study helps to determine the binding character and mineralogical forms of metals, extent of retention, and mobility/mobilization in surface sediment. Accumulation of metals in solid/sediment phases is known to occur in four major forms: exchangeable, reducible, oxidizable, and residual. These categories have different behaviors with respect to remobilization under changing environmental condition. The percentage of metal fractions in BCR extraction (Fig. 5) is in the order of residual > reducible > exchangeable > oxidizable.

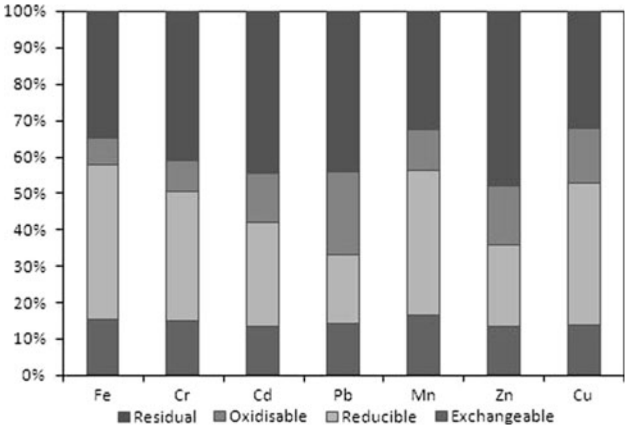

Fig. 5 BCR fractionation profile

Exchangeable fraction in BCR extraction consists of water soluble and bound to carbonate metal fractions of sediment. Mn (16.28 %) shows the highest concentration among all the metal followed by Fe (15.19 %) and Cr (14.88 %). The order of exchangeable metal fractions is Mn > Fe > Cr > Pb > Cu > Cd > Zn.

Reducible fraction of metal is the fraction bound to Fe–Mn oxides. The redox metals Fe, Mn, and Cu shows their greater/major concentration in the reducible fraction. Due to the close association of Cr with Fe–Mn oxides (Zachara et al. 1989), it also shows a significant concentration in this fraction. Reducible metal fractions show the sequence of Fe > Mn > Cu > Cr > Cd > Zn > Pb.

In oxidizable fraction, metals are bound to organic matter and sulfides. Pb, Zn, and Cu exhibit considerable amount of total content in oxidizable form, as these metals form stable and insoluble complexes with organic matter. Oxidizable fraction of metals is in the order of Pb > Zn > Cu > Cd > Mn > Cr > Fe.

Residual forms are lithogenic fraction forms of metal, which form very stable crystals. This fraction of metals in the pit pond sediment is populated highest. Cr, Cd, Pb, and Zn have their highest concentration in residual fractions, which can be explained by their lithophilic and chalcophilic nature. Residual fraction of metals follow the sequence of Zn > Cd > Pb > Cr > Fe > Mn > Cu.

The first two fractions (i.e. exchangeable and reducible forms) are less strongly bounded fraction which can easily get released to aquatic system under changing environmental conditions (i.e. change of pH, Eh, temperature, DO, etc.). Strongly bounded metal fractions, i.e. oxidizable and residual forms of metal in sediment, are resistant to remobilization. The immobile metal fraction in pit lake sediments determines the extent of virtual irreversible retention of metal in sediment (Knox et al. 2006).

The ranking of metals with respect to immobile metal fractions is in the sequence of Pb > Zn > Cd > Cr > Cu > Mn > Fe. The high recalcitrant factor (RF) for Pb, Zn, and Cd is suppose to be due to their lithophilic and chalcophilic nature, and as major fractions of these metals are in residual form. Generally, toxic heavy metals (Pb, Cd, and Cr) show higher retention in solid phases, therefore indicating poor possibility of mobilization into the aqueous system, which is consistent with previous investigations (Knox et al. 2006; Jain et al. 2008).

Regression analysis of dissolved metals with different metal fractions in sediments (Table 4) shows significant R^2 value ($P < 0.05$, 0.001) for most of the metals. This situation can be explained by the fact that retention of metals is largely associated with the proportion of strongly bounded fractions (mostly residual form) resistant to mobilize in natural systems.

Conclusion

The hydrogeochemical investigation of coal mine pit lake reveals the linkages between chemical weathering, anthropogenic inputs, which controls the chemistry of waters. Water chemistry of studied pit lake is not homogeneous and influenced by complex contamination sources and geochemical weathering process. Major ion chemistry of pit lake water reveals the dominance of alkaline earths ($Ca^{2+} + Mg^{2+}$) over alkalis ($Na^{+} + K^{+}$), and strong acids (${SO_4}^{2-} + Cl^{-}$) over the weak acids (${HCO_3}^{-}$). Weathering of Ca–Mg silicate is supposed to be the major contributor in geochemical processes. Relatively higher K_d for Cd, Pb, and Fe indicates their preferential adsorption onto the shallow-surface sediments. The major proportion of monitored metals (Cr, Pb, Cd, Zn, and Cu) is as residual fractions, except Fe and Mn showing reducible fraction as dominant form. Factor loading of measured variables resembles/accounted for geochemical weathering, anthropogenic inputs and natural/temporal factors which controls the water chemistry of pit lake.

Acknowledgments The authors wish to thank Mr. K. Pobi and Ms S. Dutta, Dept. of Chemistry, National Institute of Technology, Durgapur, for their supports during this research work.

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