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Fractionation, bioavailability, contamination and environmental risk of heavy metals in the sediments from a freshwater reservoir, Pakistan

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ABSTRACT

Fractionation of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) was studied using modified Community Bureau of Reference (mBCR) sequential extraction procedure in the sediments collected at eight sites from a freshwater lake, Pakistan. Metal fractionation showed high percentage recoveries of Cd, Co, Ni and Pb in three bioavailable fractions. The results relating potential mobility of the metals manifested following order: Cd > Pb > Ni > Co > Fe > Mn > Cr > Cu > Zn. Risk assessment code indicated medium risk for Co and Ni, medium to high for Cd and high to very high risk for Pb in the sediments. Comparison with sediments quality guidelines revealed heavy metal risk to aquatic organisms as the measured levels of Cd, Ni and Pb were higher than the prescribed levels. Enrichment factor revealed moderate enrichment for Cr, moderate to severe for Ni, severe for Co and Zn, severe to very severe for Pb and extremely severe enrichment for Cd. Contamination factor manifested moderate contamination for Co and Zn, considerable for Pb and very high contamination for Cd. In addition, pollution load index indicated high metal pollution load at a couple of sites. Spatial variability indicated relatively higher metal load at sites which were adjacent to urban and semi-urban areas. Therefore, it would be necessary to control the discharges of untreated urban/industrial wastes, agricultural runoffs and automobile emissions into the Lake.

1. Introduction

In the last few decades, much consideration has been paid to sediment pollution by heavy metals throughout the world (Selander and Svan, 2007; Zhang et al., 2007; Ramos et al., 2012). Sediments may act as metal reservoir and are responsible for transportation of essential elements and pollutants including metals in the aquatic environment (Yan et al., 2010; Davutluoglu et al., 2011; Gao and Chen, 2012). The most significant pollutants are heavy metals as they are mostly toxic, persistent and non-degradable in the aquatic ecosystems (Yang et al., 2009; Chakraborty et al., 2010; Bartoli et al., 2012; Choque et al., 2013). These metals enter the aquatic ecosystems through point sources (e.g., industrial, municipal and domestic wastes, etc.) and diffuse sources (e.g., surface runoff, soil erosion, atmospheric deposition, etc.) (Ghrefat and Yusuf, 2006; Gao et al., 2010; Passos et al., 2010; Choque et al., 2013). Their distribution is mainly influenced by nature of suspended material, anthropogenic intrusions, deposition, sorption and enrichment in organisms (Jain et al., 2007), in addition to various physicochemical characteristics (Segura et al., 2006; Rodriguez et al., 2009). With the change of environmental conditions in overlying water,

metals may be released from sediments to water. This release may result in deterioration of water quality and/or accumulation of metals in plants and animals (Zhong et al., 2006; Laing et al., 2007; Vukovic et al., 2014) and finally also humans.

Total metal levels estimation in sediments provides little information related to bioavailability, mobility, toxicity and reactivity of metals, however, they may be considered as useful indicators of metal contamination in aquatic ecosystems (Shrivastava and Banerjee, 2004; Hooda, 2010; Sundaray et al., 2011). Metal speciation in sediments is very important tool as it provides additional information related to potential mobility, bioavailability and chemical nature of a particular element (Yang et al., 2009). In recent investigations, sequential extraction procedures, using various extracting reagents and operating conditions, have been employed to get information about metals binding forms and sources in sediments (Tessier et al., 1979; Kersten and Forstner, 1986; Borovec et al., 1993; Campanella et al., 1995; Gomez-Ariza et al., 2000; Sin et al., 2001; Yang et al., 2009; Hooda, 2010; Davutluoglu et al., 2011; Sakan et al., 2016). However, it is difficult to compare the results obtained by employing these procedures. For harmonization and standardization of the sequential
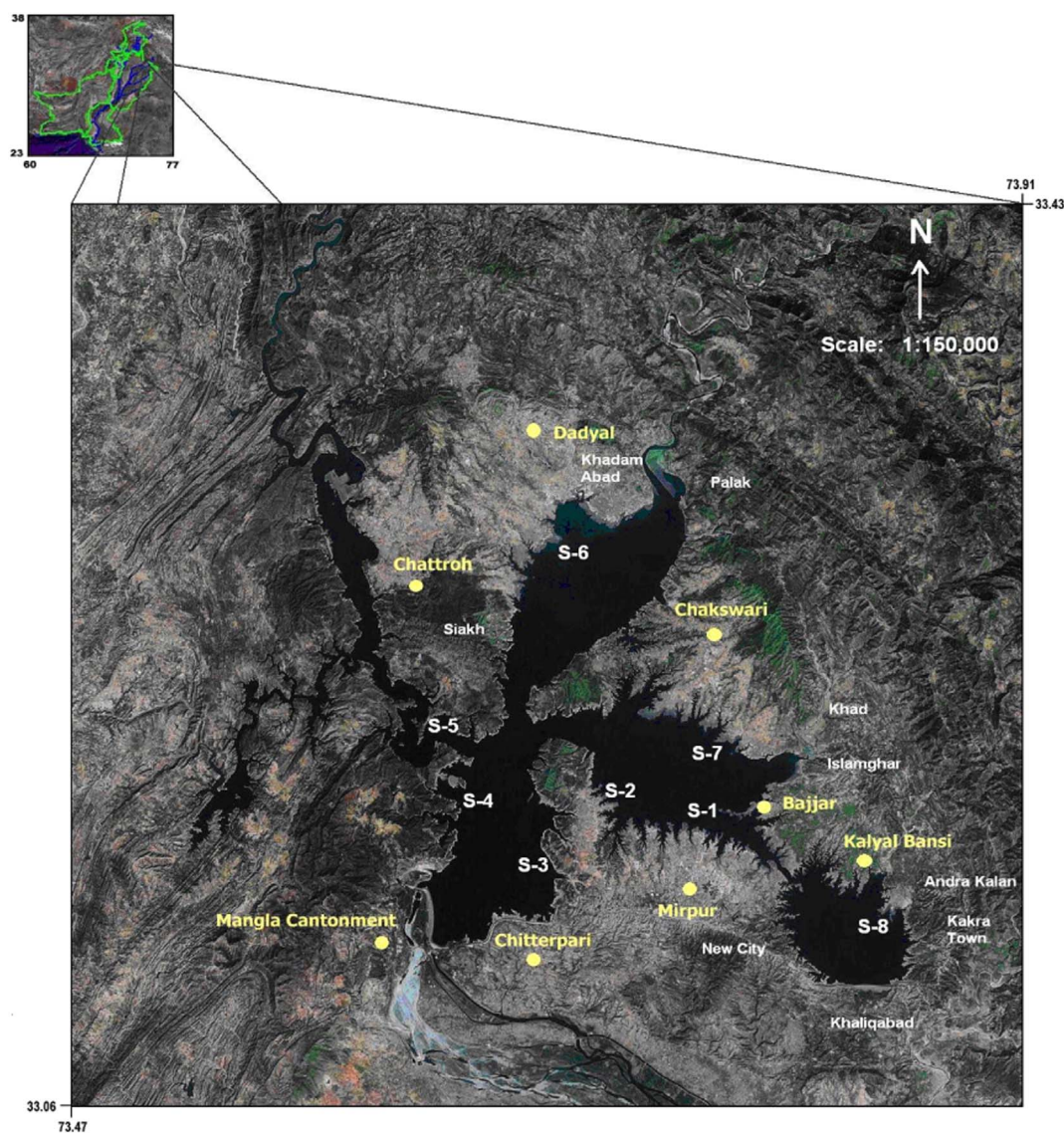
Fig. 1. Location map of the study area.

extraction procedures employed for metals speciation in soils/sediments, the Standard, Measurements and Testing Programme (formerly European Community of Bureau of Reference, BCR) has introduced a sequential extraction method (Ure et al., 1993; Davutluoglu et al., 2010; Canuto et al., 2013). This method is comprised of three extraction steps for metals speciation; exchangeable/acid soluble, reducible, and oxidisable phase. Later on, this method was altered and improved because accurate and reproducible results with acceptable certainty were difficult to be obtained by following this procedure (Rauret et al., 2001; Davutluoglu et al., 2010). In this investigation, the modified sequential extraction procedure (*m*BCR) was employed for metals speciation.

Mangla reservoir (33.12 N, 73.39 E) is one of the most important and largest freshwater resources in Pakistan (Fig. 1). It is the part of upper Indus River basin and located in the district Mirpur, Azad Jammu and Kashmir, Pakistan with maximum elevation of 630 m. The geological formations (strata) exposed in the area are dominated by continental/fluvial channel conglomerates, sandstone and floodplain shales/clays. The reservoir was constructed in 1967 by controlling the water of river Jhelum in the Pir Panjal range of upper Siwaliks. However, perennial river (Poonch) and non-perennial rivers (Kanshi and Khud) also feed the reservoir (Saleem et al., 2016). Its main purpose was to store water for irrigation and generation of hydroelectric power.

Currently, it also provides water for drinking and domestic uses in the adjoining areas. Its water surface area spreads to about 265 km^2 and is comprised of main pockets namely; Jari, Jhelum, Khad, main Mangla and Poonch (Saleem et al., 2016). The fast flowing Jhelum and Poonch rivers cut deep into the surrounding mountains and transfer large quantities of sand, silt and gravel downstream resulting into high sedimentation rates in the reservoir thereby continuously reducing storage capacity of the lake. The reservoir is surrounded by urban (Mirpur, Dadyal), semi-urban (Chakswari, Islamgarh, etc.) and village (Siakh, Palak, Panyam, Burotian, Andra Kalan, etc.) areas. Dadyal and Chakswari are located in the north, Islam Garh in the north-east, Kakra Town in the east and Mirpur City south of the Mangla dam (Ali et al., 2011; Butt et al., 2011). The reservoir is mainly polluted by untreated municipal and poultry wastes, industrial effluents and agricultural runoffs from the adjoining cities, towns and villages. Moreover, pollutants and suspended particles are also contributed by road and agricultural runoffs during rainy season (Varol, 2013).

This investigation was conducted to (i) quantify and assess spatial variations of studied elements (cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) in sediments collected from eight different locations (influential areas) in Mangla Lake, Pakistan; (ii) evaluate potential mobility

and bioavailability of the metals in various fractions of sediments using *m*BCR protocol, (iii) envisage the metal contamination through enrichment factor (EF), contamination factor (CF), pollution load index (PLI) and risk assessment code (RAC), and (iv) gauge ecotoxicological risk of the metals in sediments using sediment quality guidelines (SQGs). This investigation would offer useful information pertaining to bioavailability and contamination of the metals, and assist the environmental control actions for the anthropogenic pollutants in the studied freshwater reservoir.

2. Materials and methods

2.1. Sampling and processing

A total of eight sites, which are most influential areas, were selected for sampling of freshly deposited sediments in Mangla Lake, Pakistan during summer 2013. Samples were collected in summer when water flow in the reservoir was maximum together with relatively increased anthropogenic activities (recreational/agricultural activities) in the catchments areas. From each site, 8–10 composite samples (1–15 cm top layer) were collected with the help of a snapper (5 cm, Ø). Every composite sample was consisted of 3–5 sub-samples (covering an area of 25–50 m^2) which were well mixed and homogenized. Pre-washed zip-locked polyethylene bags were used to collect the freshly deposited sediments; and they were immediately moved to the laboratory by using ice-cold cooler (Saleem et al., 2016). Composite sampling was carried out to cover more area with least number of samples, get more knowledge about mean pollutant levels, highlight the hot spots, precise hotspots concentrations and reduce the sampling cost (USEPA, 1991; Carson, 2001; Correll, 2001; Saleem et al., 2013). Stones, granules and debris were separated manually (Nemati et al., 2011). After drying (at 85 °C in an electric oven for 48 h), grinding (by mortar), mixing and sieving through 2 mm nylon mesh (< 2000 μm grain size), the sediments were stored in pre-washed polyethylene bags and placed in a refrigerator (Kannan et al., 2008; Saleem et al., 2016).

2.2. Physicochemical characterization

A suspension of sediment in de-ionized water (1:2 ratio) was prepared for determination of TDS (total dissolved solids), EC (electrical conductivity) and pH (hydrogen ion concentration). Total dissolved solids, pH and EC were estimated in the suspension after resting for 10 min by using a multimeter (Bench Meter, Martini Instrument Mi 180) (Radojevic and Bashkin, 1999; Bartoli et al., 2012; Saleem et al., 2016). The sediments were heated at 550 °C for determining organic matter (OM, %) by following weight loss method (Diaz-de-Alba et al., 2011; Saleem et al., 2016).

2.3. Analytical techniques

2.3.1. Reagents and glassware

The glassware was processed to remove any contamination according to Diaz-de-Alba et al. (2011) and Saleem et al. (2016). Fresh working standards were prepared from successive dilution of the standard metal solutions (1000 mg/L) with de-ionized water.

2.3.2. Pseudo total metal digestion

For bulk metal analysis, sediments (1–2 g, dry weight, < 2000 μm grain size) placed in pre-cleaned glass vessel were allowed to react with 20 mL of freshly prepared solution of HNO$_3$ and HCl (3:1 ratio) by using a microwave oven system (USEPA, 2007; Choque et al., 2013). Blanks having all reagents without sediment samples were also treated in the same way along with each batch. Fine filters (0.45 μm, pore size) were used for the filtration of the digests. Then, the extracts were diluted with de-ionized water (with resistivity of 18 MΩ/cm) and kept at 4 °C until metal analysis was carried out (Saleem et al., 2014a).

2.3.3. Sequential extraction procedure

Three steps modified BCR (*m*BCR) procedure along with residual fraction was applied for sequential extraction (Davutluoglu et al., 2010; Passos et al., 2010; Nemati et al., 2011). The detailed description of the extraction procedure was as follows:

Stage 1, Fraction 1 (F1, acid soluble/exchangeable fraction): about 1 g of dried sediments placed in 50 mL Pyrex vessels were allowed to react with 40 mL solution of 0.11 M acetic acid (CH$_3$COOH) at ambient conditions, and agitated for 16 h using an auto-shaker at 320 rotations per minute (Choque et al., 2013). Then, the solution was centrifuged at 3000 rpm for 20 min, and the supernatant separated by decantation was stored for afterward metal analysis. The residue was rinsed with deionised water (20 mL), agitated for 20 min on an auto-shaker and centrifuged at 3000 rpm for 20 min. Subsequently, the supernatant was decanted.

Stage 2, Fraction 2 (F2, reducible fraction): the residue from stage 1, placed in the Pyrex vessel, was agitated with 40 mL of 0.5 M hydroxylammonium chloride solution (pH 1.5) for 16 h at ambient conditions on an auto-shaker at 320 rpm. The remaining steps such as centrifugation, supernatant collection, and residue rinsing were similar to that mentioned in the stage 1 (Nemati et al., 2011).

Stage 3, Fraction 3 (F3, oxidisable fraction): the residue from stage 2, placed in the Pyrex vessel, was treated with 10 mL hydrogen peroxide (H$_2$O$_2$) solution (8.8 M, pH 2–3) at ambient conditions for 1 h with slight manual agitation. The vessel was loosely capped to prevent substantial loss of H$_2$O$_2$. Then, it was heated at 85 ± 2 °C for 1 h by using a water bath to reduce its volume to 2–3 mL. Afterwards, the mixture was treated with 10 mL solution of 8.8 M H$_2$O$_2$, heated again at 85 ± 2 °C for 1 h to reduce its volume near to dryness, cooled, and allowed to react with 50 mL solution of ammonium acetate (1.0 M, pH 2) while shaking at 320 rpm at ambient conditions for 16 h. The remaining steps were similar as discussed above (Choque et al., 2013; Sakan et al., 2016). Blanks having all reagents without samples were processed with every batch.

Stage 4, Fraction 4 (F4, residual fraction): the residue obtained from stage 3, placed in Pyrex vessel, was treated with 10 mL solution of freshly prepared aqua regia. The mixture was kept for 16 h at ambient conditions for slow dissolution of residual sediment, and then heated slowly to reflux conditions which were maintained for 2 h. The extract was separated by filtration through fine filters (0.45 μm), and the residue on the filters was rinsed with 0.5 M nitric acid (HNO$_3$) solution and the final volume (50 mL) was adjusted with 0.5 M HNO$_3$ solution (Nemati et al., 2011; Passos et al., 2010; Sakan et al., 2016). The fourth step (residual fraction) was included for quality control and comparison of sequential extraction results with pseudo-total metal analysis results by internal check recovery method (Davutluoglu et al., 2010).

2.3.4. Quantification of heavy metals

Heavy metal (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) levels were quantified by using flame atomic absorption spectrophotometer in calibration line mode (Shimadzu AA-670, Japan), and the digest dilutions were made appropriately whenever required (Radojevic and Bashkin, 1999). Triplicate absorbance readings were measured. Analyses were carried out following analytical conditions described in Saleem et al. (2016).

2.3.5. Quality control/assurance

The quality assurance for pseudo total metal analysis was maintained by analysing SRM-2709 (San Joaquin Soil), yielding good accuracy of analysis (94–106%, *n* = 3). Conversely, BCR-701 (Lake Sediment, *n* = 3) was analysed to ensure the validity and quality of sequential extraction procedure. The measured elemental levels were compared with their reference concentrations, and mean recovery (%) was computed by comparing the measured levels with the certified values as shown in Table 1. Moreover, reagent blanks were also prepared during pseudo total metal digestion and sequential extractions in

Table 1
Mean recoveries (n = 3) of standard sediment reference material BCR-701 (Lake Sediment) by applying BCR sequential extraction method.

	Fraction 1 (%)	Fraction 2 (%)	Fraction 3 (%)	Residual fraction (%)
Cd	102 ± 3	103 ± 3	109 ± 6	114 ± 2
Cr	109 ± 5	100 ± 3	97 ± 3	105 ± 3
Cu	95 ± 5	99 ± 5	105 ± 4	109 ± 5
Ni	103 ± 3	98 ± 4	103 ± 4	105 ± 3
Pb	104 ± 5	99 ± 6	103 ± 6	105 ± 4
Zn	95 ± 4	101 ± 5	104 ± 7	108 ± 3

the same manner to avoid gross contamination and to ensure reliability of the metal analysis (Passos et al., 2010).

The efficiency of the method and the precision of the results obtained were checked by calculating the ratio between the sum of metals concentrations obtained by various reagents using sequential extraction procedure and the pseudo total metal concentrations (Nemati et al., 2011; Yang et al., 2015). The internal check recovery of the sequential extraction procedure was computed by the following equation:

$$\text{Recovery (\%)} = \left(\frac{C_{ex} + C_{red} + C_{ox} + C_{res}}{C_{pseudototal}} \right) \times 100 \tag{1}$$

where C_{ex}, C_{red}, C_{ox}, C_{res} and $C_{pseudototal}$ refers to the metals concentration in exchangeable, reducible, oxidisable, residual and pseudototal fractions, respectively. Generally, the recovery results (94–106%) showed a good and acceptable agreement between metal levels extracted by the two different procedures (Choque et al., 2013).

2.4. Ecological risk assessment

2.4.1. Sediments quality guidelines (SQGs)

These guidelines are used to assess sediments pollution by associating the measured pollutant levels with the matching guidelines and to evaluate the influence of pollutants on the aquatic biota (MacDonald et al., 2000; Zheng et al., 2008; Varol, 2011). These are highly useful for monitoring strategies, inferring ancient data, sediment quality evaluations, environmental risk evaluation, remedial investigations and designing the sediment quality goals (MacDonald et al., 2000; Farkas et al., 2007; Zheng et al., 2008; Varol, 2011; Li et al., 2013). In present investigation, combination of two types of sediment quality guidelines were used to evaluate the environmental risk of element levels in the examined sediments, namely; i) lowest effect level (LEL)/severe effect level (SEL) and ii) the threshold effect level (TEL)/probable effect level (PEL) (MacDonald et al., 2000; Davutluoglu et al., 2011; Saleem et al., 2016). The LEL & TEL define the concentrations below which harmful influences on overlying flora and fauna would be unlikely or rare. In contrast, harmful influences would be likely observed when elemental levels would be higher than the SEL & PEL (Davutluoglu et al., 2011).

2.4.2. Enrichment factor (EF)

Effect of anthropogenic activities on the sediments is assessed by EF which requires a normalizing metal (Choque et al., 2013) for mitigating the disparities arisen by heterogeneous nature of sediments (Saleem et al., 2013). As Fe has absorbing ability for the metals, and it is also linked with fine solid surfaces, it was considered as a reference metal. Moreover, it is present in much higher concentrations, associated with fine-grained aluminosilicates and is a quasiconservative tracer of element-absorbing phases (Daskalakis and O'Connor, 1995; Delgado et al., 2012; Hassan et al., 2013). In present investigation, Fe showed significantly strong correlations (n = 70, critical r = 0.277) with most of the metals including Co (r = 0.748), Mn (r = 0.674), Cu (r = 0.670), Zn (r = 0.610) and Cr (r = 0.610), thus validating its choice as normalization element. EF is calculated by using the following equation:

$$EF = \frac{[X/Fe]_{sample}}{[X/Fe]_{crust}} \tag{2}$$

where $[X/Fe]_{sample}$ and $[X/Fe]_{crust}$ denote the ratios between average levels (mg/kg, dry weight) of the marked element (X) and Fe in the examined sediments and continental earth crust, respectively (Lide, 2005).

2.4.3. Contamination factor (CF) and pollution load index (PLI)

These pollution indices were applied in order to gauge the anthropogenic elemental pollution (Abrahim and Parker, 2008; Iqbal and Shah, 2011). For individual element, CF was calculated by comparing the estimated levels in the examined sediments with the earth crust value by using the following equation:

$$CF = \frac{C_{sample}}{C_{crust}} \tag{3}$$

where C_{sample} and C_{crust} denote the average levels (mg/kg, dry weight) of the marked element in the examined sediments and continental earth crust (Lide, 2005).

Pollution load index (PLI) is an easy and reasonable way for determining the metals cumulative pollution, and it is computed as the nth root of the n contamination factors (CFn) multiplied together by using the following relationship (Tomlinson et al., 1980; Varol, 2011; Saleem et al., 2016):

$$PLI = (CF1 \times CF2 \times CF3 \times \cdots\cdots \times CFn)^{\frac{1}{n}} \tag{4}$$

2.4.4. Risk assessment code (RAC)

Effects of metals on the aquatic biota can be measured by various types of sediment quality evaluation techniques including RAC index (Davutluoglu et al., 2011). The bioavailability and adverse effects of the metals on the biota depend upon their binding strength with different chemical phases in the aquatic ecosystems (Kouassi et al., 2014). The RAC (%) is calculated by comparing the concentration in exchangeable fraction (F1) with levels determined in other geochemical fractions (F2 + F3 + F4) (Perin et al., 1985; Passos et al., 2010; Yu et al., 2011).

$$RAC (\%) = \left(\frac{F1}{F2 + F3 + F4} \right) \times 100 \tag{5}$$

3. Result and discussion

3.1. Physicochemical characteristics

Average variations in the physicochemical characteristics of surface sediments from Mangla Lake, Pakistan are shown in Table 2. Buffering capacity of the sediments controls pH based bioleaching process of contaminated sediments in addition to other physicochemical processes. Elements may be released into water column from sediments

Table 2
Statistical summary of physicochemical parameters in sediments from different sites (n = 70).

	pH	EC (μS/cm)	TDS (mg/L)	OM (%)
S-1	7.40	503	252	4.45
S-2	7.54	384	192	7.42
S-3	7.41	475	237	4.42
S-4	7.29	567	284	5.98
S-5	7.06	464	232	6.65
S-6	7.28	495	248	4.14
S-7	7.29	456	228	7.42
S-8	7.58	393	196	7.64
Mean	7.36	467	234	5.96
Median	7.29	472	236	6.57
SD	0.30	141	71	1.66

when pH value changes (Bartoli et al., 2012). In current investigation, nearly neutral pH (7.06–7.58) was noted in the examined sediments. The lower pH (7.1) was noted at site S-5, whereas the higher value (7.58) in sediments collected from S-8. The results of the present study were considerably different from those of an earlier study, which showed slightly acidic nature of the sediments in Mangla Lake during summer and winter (Saleem et al., 2013); however, another study reported slightly alkaline nature of water in the reservoir (Saleem et al., 2014b). So it can be assumed that the pH is variable and may affect the bioleaching.

Total dissolved solids (TDS) and electrical conductivity (EC) levels ranged from 192 to 284 mg/L and 384–567 µS/cm, respectively. In general, texture of the sediments was sandy loam. Organic matter (OM) is considered very significant for retaining heavy elements in sediments, plying very important role in determination of sediments quality (Saleem et al., 2016). Its levels indicated some fluctuations at most of the sites and varied from 4.14–7.64%. Relatively higher concentrations of OM were noted at sites S-8, S-7 and S-2 which might be introduced into sediments by untreated domestic and urban wastes (Li et al., 2000; Choque et al., 2013; Saleem et al., 2016). In this study the OM input sources might be Mirpur city, Kakra town, Kalyal Bensi, Andra Kalan, Islamghar and Khad surrounding these sites.

3.2. Pseudo-total metal concentrations in sediments

The pseudo-total concentrations for all studied metals at eight different sites are given in Table 3. The ranges of metal concentrations at all sites were: 2.93–8.48 mg/kg for Cd, 20.3–54.3 mg/kg for Co, 28.2–35.7 mg/kg for Cr, 22.6–39.9 mg/kg for Cu, 4066–5046 mg/kg for Fe, 325–443 mg/kg for Mn, 26.9–72.0 mg/kg for Ni, 40.4–72.3 mg/kg for Pb and 84.2–178 mg/kg for Zn. In the current study, total metal contents at different sites followed the order: S-1 > S-2 > S-3 > S-6 > S-8 > S-4 > S-7 > S-5. The sites S1-S3 and S-6 were found to have relatively higher levels of studied metals. Sampling sites S1-S3 receive untreated urban and industrial waste waters from the city area; while site S6 receive untreated domestic waste waters from small city (Dadyal), town (Panyam) and agricultural run-offs from the nearby villages. The lowest metal values were found at site S5 close to the mouth of the Jhelum River. One of the earlier studies from Mangle Lake also reported noteworthy spatial variations in the water samples; elevated metal levels were found near the urbanized areas while the samples from remote areas exhibited relatively low metal contents (Saleem et al., 2015).

The different types of the sediments quality guidelines were applied to this study. TEL-threshold effects level, PEL-probable effects level, LEL-lowest effect level, and SEL-severe effect level are given in Table 4. The measured levels of Cd, Cr, Cu, Ni and Pb were between LEL and SEL values in 100% samples, whereas Zn contents were between LEL and SEL values in 62.5% of the samples. However, the selected metals concentrations did not exceed SEL value. Compared with TEL and PEL values, Cr, Cu and Zn concentrations were lower than TEL in 100%, 87.5% and 50% of the samples, respectively. The measured levels of Cd and Ni exceeded the PEL in 62.5% of the samples whereas Pb concentrations were between TEL and PEL in 100% of the samples. Consequently, Cd and Ni are metals which can potentially be harmful to aquatic organisms in the Mangla Lake as their concentrations at most of the sites were above the PEL value, indicating their frequent potential toxicity for aquatic organisms. Nevertheless, Pb, Cr and Cu may also cause adverse biological effects as their levels also exceeded the LEL levels in 100% of sediment samples. Moreover, Zn concentrations exceeded LEL and TEL values in > 50% of the samples, showing its potential toxicity for aquatic biota in the water reservoir.

An earlier study in the water reservoir had revealed moderate pollution caused by Cd, Cr, Cu and Pb in the sediments and the extent of pollution was relatively higher during winter than during summer (Saleem et al., 2013). Similarly, another study manifested that mean

levels of Cd, Co, Cr, Ni and Pb in the water samples from Mangla Lake were elevated as compared to the national and international allowable limits (Saleem et al., 2014b).

3.3. Speciation of selected metals in sediments

The average values of selected elements pertaining to various geochemical phases of the sediments from all sampling stations, shown in Table 3, followed the sequence:

Cd: Exchangeable > Oxidisable > Reducible > Residual
Co: Residual > Reducible > Exchangeable > Oxidisable
Cr: Residual > Oxidisable > Reducible > Exchangeable
Cu: Residual > Reducible > Exchangeable > Oxidisable
Fe: Residual > Reducible > Oxidisable > Exchangeable
Mn: Residual > Reducible > Exchangeable > Oxidisable
Ni: Reducible > Exchangeable > Oxidisable > Residual
Pb: Exchangeable > Reducible > Residual > Oxidisable
Zn: Residual > Reducible > Oxidisable > Exchangeable

Among the studied elements, Zn (87.2–94.7%), Cu (64.3–84.0%), Cr (60.1–76.9%), Mn (47.6–59.0%), Fe (45.9–53.9%), and Co (35.1–67.6%) showed dominant levels in residual fraction of the sediments as shown in Fig. 2. The organic bound (oxidisable) fraction of Cd and Ni were found to be significant, while the oxidisable fraction of Co, Cr, Cu, Fe, Mn and Zn were geo-chemically insignificant (< 14% of total). The insignificant levels of Fe and Mn may be due to hydrous Fe-Mn oxide forms and Fe-Mn organic complex (Sundaray et al., 2011). Moreover, the exchangeable fractions of Fe and Zn were statistically insignificant (< 1% of total) in the sediments.

The exchangeable and carbonate bound fractions (weakly bound forms) are partially introduced by anthropogenic intrusions. These fractions may be leached very easily in water column, and may cause potential harm to the aquatic species. The increasing oxidizing conditions may dissolve Fe–Mn oxides and the organic matter fractions (Karbassi and Shankar, 2005; Sundaray et al., 2011). The residual fractions are considered to be contributed mainly by geogenic sources (Salmonas and Forstner, 1980; Islam et al., 2015). The bioavailable fractions (sum of first three fraction, F1 + F2 + F3), solubilized at favourable conditions of pH and redox potential, may cause adverse effects to benthic flora and fauna (Sundaray et al., 2011). The bioavailable (Passos et al., 2010) fractions of selected metals in each site are presented in Table 5. In this study, mobility sequence of the metals was Cd > Pb > Ni > Co > Fe > Mn > Cr > Cu > Zn. In general, concentrations of Fe and Mn are found to be higher in the sediments, and their higher levels in bioavailable fraction might be due to metal carbonates and oxides formation (Carroll et al., 2002; Sundaray et al., 2011; Choque et al., 2013). Sedimentary geochemical speciation data of the metals suggested that among the mobile fractions, high values of Cd (73–93%), Pb (70–97%), Ni (61–91%) and Co (32–65%) in the bioavailable fractions (F1 + F2 + F3) might have adverse biological effects on aquatic biota in the Lake. Comparatively higher potential bioavailability of Cd was found at sites S2, S7 and S8; Pb at S6-S8; Ni at S1, S6 and S7; and Co at S1, S2, S4 and S8. Commonly, the elevated metal concentrations in exchangeable and Fe-Mn oxides–bound fractions of sediments might be due to anthropogenic intrusions (as most of the metal oxides are water insoluble), and are considered more bioavailable (Filgueiras et al., 2004; Farkas et al., 2007; Yu et al., 2011).

The elevated levels of Cd, Ni, Pb and Co in bioavailable fraction might be introduced by anthropogenic intrusions, such as agricultural practices, automobile exhausts, untreated domestic and industrial wastes (Farkas et al., 2007; Iqbal et al., 2013; Filgueiras et al., 2004). In the current investigation, Cd, Pb, Ni and Co were noted to be highly mobile and their high concentrations in the bioavailable fractions might cause serious environmental concerns.

Table 3
Metal concentrations (mg/kg, dry weight) in sediments obtained by mBCR sequential extraction method and by pseudototal digestion.

Site	Fraction	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
S-1	Exchangeable	1.21	3.65	1.35	1.97	14.7	82.0	7.80	15.9	0.53
	Reducible	0.51	11.7	3.01	4.01	2461	81.4	23.7	14.0	7.21
	Oxidisable	0.83	3.78	4.37	0.73	226	18.6	7.28	3.69	2.27
	Residual	0.93	16.2	24.6	31.2	2294	262	3.76	14.4	75.0
	Total (Fl:F4)	3.48	35.3	33.3	37.9	4995	444	42.6	47.9	85.0
	Pseudo total	3.51	35.0	34.7	39.9	5045	431	43.4	46.1	84.2
	Recovery (%)	99	101	96	95	99	103	98	104	101
S-2	Exchangeable	2.30	7.94	1.85	1.85	21.6	79.6	17.7	21.4	0.13
	Reducible	1.45	19.6	5.04	1.99	1979	101	24.4	9.21	10.8
	Oxidisable	1.67	3.96	5.42	0.30	249	16.8	6.49	0.70	2.02
	Residual	0.42	22.3	22.3	23.3	2235	235	4.26	11.5	123
	Total (Fl:F4)	5.84	53.8	34.6	27.4	4484	432	52.8	42.8	136
	Pseudo total	6.08	54.3	34.0	28.0	4623	428	55.6	40.4	133
	Recovery (%)	96	99	102	98	97	101	95	106	102
S-3	Exchangeable	1.41	1.99	1.36	2.91	20.2	85.1	12.8	20.1	0.92
	Reducible	0.64	9.06	2.09	2.65	2222	111	15.4	13.0	11.1
	Oxidisable	0.48	2.34	3.47	1.55	209	17.96	7.86	2.66	1.99
	Residual	0.52	13.3	23.1	23.7	2288	213	9.09	8.61	155
	Total (Fl:F4)	3.06	26.7	30.0	30.8	4739	427	45.1	44.3	169
	Pseudo total	3.02	27.5	28.9	32.1	4514	436	44.7	44.8	178
	Recovery (%)	101	97	104	96	105	98	101	99	95
S-4	Exchangeable	2.25	8.58	4.92	2.75	26.37	79.5	18.2	20.9	0.06
	Reducible	1.27	16.5	4.45	2.90	1886	100	31.1	12.8	5.67
	Oxidisable	0.45	4.62	4.75	1.18	155	19.6	13.7	1.77	0.60
	Residual	0.70	16.1	21.2	18.1	2266	230	11.2	8.74	113
	Total (Fl:F4)	4.67	45.8	35.3	24.9	4333	430	74.2	44.2	119
	Pseudo total	4.77	46.3	35.7	24.2	4290	438	72.0	43.36	115
	Recovery (%)	98	99	99	103	101	98	103	102	103
S-5	Exchangeable	0.63	4.02	3.23	1.08	26.3	86.4	6.03	23.8	0.67
	Reducible	0.38	1.58	4.16	5.95	1608	53.9	9.11	10.2	9.84
	Oxidisable	1.18	1.61	3.11	0.43	224	15.9	4.67	3.17	2.19
	Residual	0.77	15.0	19.6	19.2	2168	221	12.8	9.22	110
	Total (Fl:F4)	2.96	22.3	30.1	26.7	4025	377	32.6	46.4	122
	Pseudo total	2.93	21.8	28.6	27.5	4066	370	33.0	47.4	121
	Recovery (%)	101	102	105	97	99	102	99	98	101
S-6	Exchangeable	1.77	6.51	2.25	1.25	26.4	77.1	13.0	27.2	0.05
	Reducible	0.62	6.69	3.69	3.62	1985	93.0	19.1	11.3	10.7
	Oxidisable	1.67	3.39	3.92	0.40	180	14.7	7.33	6.09	3.11
	Residual	0.75	18.0	19.2	17.1	2130	168	6.14	7.44	94.8
	Total (Fl:F4)	4.82	34.6	29.0	22.4	4320	353	45.6	52.1	109
	Pseudo total	5.02	34.9	28.2	22.6	4550	363	45.1	54.2	104
	Recovery (%)	96	99	103	99	95	97	101	96	105
S-7	Exchangeable	0.47	2.95	3.08	1.87	11.7	67.3	6.67	16.7	0.15
	Reducible	1.13	7.83	1.41	4.37	1960	62.1	9.80	25.8	8.38
	Oxidisable	5.33	0.16	2.52	1.00	191	14.9	7.29	4.15	3.20
	Residual	0.73	10.2	20.3	17.3	2189	175	4.18	3.19	117
	Total (Fl:F4)	7.66	21.1	27.3	24.5	4352	319	27.9	49.8	129
	Pseudo total	7.74	20.3	29.0	24.2	4225	325	26.9	50.3	128
	Recovery (%)	99	104	94	101	103	98	104	99	101
S-8	Exchangeable	1.55	5.60	4.97	4.12	17.4	86.1	9.07	37.8	0.04
	Reducible	0.93	15.8	3.27	5.35	1879	90.3	12.5	28.4	7.87
	Oxidisable	5.55	0.60	4.12	0.82	199	15.9	3.90	6.97	2.45
	Residual	0.63	14.9	20.8	18.5	2252	224	6.35	2.04	109
	Total (Fl:F4)	8.65	36.8	33.2	28.8	4346	417	31.8	75.2	120
	Pseudo total	8.48	34.8	32.9	29.1	4303	443	32.5	72.3	125
	Recovery (%)	102	106	101	99	101	94	98	104	96

Table 4
Comparison between sediment quality guidelines (SQGs) with selected metal concentrations (mg/kg) in sediments.

	Cd	Cr	Cu	Ni	Pb	Zn
LEL	0.6	26	16	16	31	120
SEL	10	110	110	75	250	820
TEL	0.596	37.3	35.7	18	35	123
PEL	3.53	90	197	36	91.3	315
Samples < LEL (%)	0	0	0	0	0	37.5
Samples LEL-SEL (%)	100	100	100	100	100	62.5
Samples > SEL (%)	0	0	0	0	0	0
Samples < TEL (%)	0	100	87.5	0	0	50
Samples TEL-PEL (%)	37.5	0	12.5	37.5	100	50
Samples > PEL (%)	62.5	0	0	62.5	0	0

3.4. Enrichment factor (EF)

The EF values were inferred as suggested by Sakan et al. (2009): EF < 1 indicates no enrichment, EF < 3 minor enrichment, EF 3–5 moderate enrichment, EF 5–10 moderately severe enrichment, EF 10–25 severe enrichment, EF 25–50 very severe enrichment, and EF > 50 extremely severe enrichment. The mean EF values of the metals at all sites are shown in Table 6 where the decreasing order was noted as Cd > Pb > Zn > Co > Ni > Cu > Mn > Cr. Almost similar trend was reported in an earlier study (Saleem et al., 2016). The EF results showed moderate enrichment for Cr, moderate enrichment to moderately severe enrichment for Cu, Ni and Mn and severe enrichment for Zn and Co. Cadmium and Pb showed severe to very severe enrichment and extremely severe enrichment, respectively, due to

Fig. 2. The percentages of metal fractionations in sediments at different sites (S-1 to S-8).

Table 5
Contribution of the metals (%) in bioavailable fractions of sediments at different sites.

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
S-1	73.4	54.1	26.2	17.7	54.1	41.0	91.2	70.0	11.8
S-2	92.7	58.5	35.5	15.1	50.2	45.7	73.1	73.1	9.55
S-3	83.1	50.3	23.1	23.1	51.7	50.0	79.9	80.6	8.26
S-4	85.0	64.9	39.9	27.4	47.7	46.4	81.5	80.2	5.33
S-5	74.2	32.4	34.9	28.0	46.1	41.4	60.7	80.1	10.4
S-6	84.5	48.0	33.9	23.6	50.7	52.4	86.5	85.7	12.8
S-7	90.5	51.8	25.7	29.5	49.7	45.2	85.0	93.6	9.10
S-8	92.8	59.6	37.2	35.7	48.2	46.2	80.1	97.3	8.65
Min	73.4	32.4	23.1	15.1	46.1	41.0	60.7	70.0	5.33
Max	92.8	64.9	39.9	35.7	54.1	52.4	91.2	97.3	12.8
Mean	84.5	52.5	32.1	25.0	49.8	46.0	79.7	82.6	9.48

Table 6
Contamination factors (CF), pollution load index (PLI), enrichment factors (EF) and RAC (%) results for selected metals at different sites.

		S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	Average
CF	Cd	23.4	40.5	20.2	31.8	19.5	33.4	51.6	56.5	34.6
	Co	1.40	2.17	1.10	1.85	0.87	1.40	0.81	1.39	1.37
	Cr	0.34	0.33	0.28	0.35	0.28	0.28	0.28	0.32	0.31
	Cu	0.66	0.47	0.53	0.40	0.46	0.38	0.40	0.49	0.47
	Fe	0.09	0.08	0.08	0.08	0.07	0.08	0.08	0.08	0.08
	Mn	0.45	0.45	0.46	0.46	0.39	0.38	0.34	0.47	0.43
	Ni	0.52	0.66	0.53	0.86	0.39	0.54	0.32	0.39	0.53
	Pb	3.29	2.89	3.20	3.10	3.38	3.87	3.60	5.17	3.56
	Zn	1.20	1.90	2.54	1.65	1.73	1.48	1.82	1.78	1.76
	PLI	0.95	1.07	0.93	1.03	0.80	0.92	0.86	1.05	0.95
EF	Cd	261	494	251	417	270	414	687	739	442
	Co	15.6	26.5	13.7	24.3	12.1	17.3	10.8	18.2	17.3
	Cr	3.80	4.05	3.53	4.59	3.89	3.42	3.79	4.22	3.91
	Cu	7.42	5.67	6.67	5.29	6.34	4.66	5.38	6.35	5.97
	Mn	5.06	5.49	5.72	6.05	5.39	4.74	4.56	6.10	5.39
	Ni	5.77	8.05	6.63	11.2	5.43	6.65	4.26	5.06	6.64
	Pb	36.7	35.1	39.9	40.6	46.9	47.9	47.9	67.6	45.3
	Zn	13.4	23.2	31.7	21.6	24.0	18.3	24.3	23.3	22.5
RAC (%)	Cd	34.8	39.3	46.3	48.1	21.4	36.8	6.09	17.9	31.3
	Co	10.3	14.8	7.48	18.7	18.1	18.8	14.0	15.2	14.7
	Cr	4.05	5.33	4.54	13.9	10.7	7.73	11.3	15.0	9.07
	Cu	5.19	6.74	9.45	11.0	4.04	5.58	7.62	14.3	8.00
	Fe	0.29	0.48	0.43	0.61	0.65	0.61	0.27	0.40	0.47
	Mn	18.5	18.4	19.9	18.5	22.9	21.9	21.1	20.7	20.2
	Ni	18.3	33.4	28.3	24.5	18.5	28.5	23.9	28.5	25.5
	Pb	33.2	50.0	45.4	47.2	51.3	52.3	33.6	50.3	45.4
	Zn	0.62	0.09	0.54	0.05	0.54	0.04	0.12	0.03	0.26

anthropogenic inputs at all sites. More or less similar enrichment results for the metals were reported earlier from the study area (Saleem et al., 2013).

3.5. Contamination factor (CF) and pollution load index (PLI)

CF values were inferred as proposed by Hakanson (1980): CF < 1 indicates low contamination; 1 < CF < 3 indicates moderate contamination; 3 < CF < 6 indicates considerable contamination; and CF > 6 indicates very high contamination (Montuori et al., 2013). The mean CF and PLI results of the selected metals in the sediments are shown in Table 6. Contamination factor results showed low contamination for Cr, Cu, Fe, Ni, and Mn; moderate contamination for Zn and Co; considerable contamination for Pb; and very high contamination for Cd.

The PLI value > 1 indicates a polluted condition, while PLI < 1 means no metal pollution existing (Tomlinson et al., 1980; Varol, 2011). The PLI results indicated metal pollution at all sites in the Mangla Lake. However, higher PLI levels were found for sites S-2 and S-8 and minimum for site S-5. Sites S-2 and S-8 exhibited higher PLI levels as these sites collect untreated municipal and industrial wastes from Mirpur city and adjacent regions (Saleem et al., 2016).

3.6. Risk assessment code (RAC)

From ecological point of view, exchangeable phase is very significant as metals bound to this fraction may easily be leached in neutral or slightly acidic waters (Filgueiras et al., 2004), and they may be accumulated by living organisms. Thus, the fraction (F1) may be used for evaluating the potential adverse effects on the organisms (Delgado et al., 2011; Guillen et al., 2012). The RAC (%) may be computed by comparing the metal concentrations in exchangeable phase (F1) with total metal levels. The RAC values were interpreted as: no risk (< 1%), low risk (1–10%), medium risk (11–30%), high risk (31–50%), and very high risk (> 50%), which is considered dangerous as metals easily enter the food chain (Perin et al., 1985; Passos et al., 2010; Yu et al., 2011). The comparative evaluation of RAC values (%) in sediments at different sites is given in Table 6. The RAC results manifested no risk for Fe and Zn; low to medium risk for Cr and Cu; medium risk for Co, Mn and Ni; medium to high risk for Cd; and high to very high risk for Pb. The highest RAC values for Ni and Co were found at sites S-2 and S-6, respectively; and Pb manifested high risk at sites S-1 to S-4 and S-7 and very high risk at S-5, S-6 and S-8. The highest RAC values were found for Pb (52.3%), Cd (48.1%), Ni (33.4%) and Co (18.8%) at S-6, S-4, S-2 and S-6, respectively. Consequently, Cd, Ni, Co and Pb were considered dangerous for the aquatic flora and fauna. Saleem et al. (2014b) reported almost similar findings for human health risk associated with water consumption from the reservoir. Hence, Cd, Co, Ni and Pb intrusions into the reservoir should be controlled as a priority (Nemati et al., 2011).

4. Conclusions

In this study, the *m*BCR sequential extraction method was practiced to study the fractionation of studied metals in surface sediments from Mangla Lake, Pakistan. The sediments were somewhat contaminated with anthropogenic heavy metals (Cd, Co, Ni and Pb) with significant mobility/availability. Due to greater values of bioavailable fractions (F1 + F2 + F3), metals Cd, Co, Ni and Pb could pose potential environmental risk. Moreover, Cd and Pb, as well as Ni and Co showed noteworthy proportions of recoveries in the exchangeable fraction (F1). Hence, Cd and Pb presented serious risk to aquatic biota particularly because they are very toxic and may accumulate in the overlying flora and fauna. The metals bioavailability showed the following trend: Cd > Pb > Ni > Co > Fe > Mn > Cr > Cu > Zn. According to risk assessment code (RAC, %), Co and Ni presented medium risk; Cd showed medium to high risk; and Pb indicated high to very high risk. The highest RAC values were found for Pb (52.3%), Cd (48.1%), Ni (33.4%) and Co (18.8%) at sites S-6, S-4, S-2 and S-6, respectively. Ecological hazard assessment using sediment quality guidelines (SQGs) showed possible heavy metal risk to aquatic organisms as the measured concentrations of most of the metals (Cd, Co, Ni and Pb) were greater than the lowest effect levels, threshold effect levels and probable effect levels; enrichment factor (EF) results revealed moderate enrichment for Cr, moderate to severe enrichment for Ni, severe enrichment for Co and Zn, severe to very severe enrichment for Pb and extremely severe enrichment for Cd; contamination factor (CF) manifested moderate contamination for Co and Zn, considerable for Pb and very high contamination for Cd; and pollution load index (PLI) indicated high metal pollution load at sites S-2 and S-8, which were close to Mirpur city and adjacent areas. Overall, environmental risk analyses of the studied metals presented a very high ecological risk at the sites that were near to Mirpur city and adjacent areas (S-1 to S-3, S-6 and S-8), while low ecological risk was found in the less populated areas (S-4 and S-5). Therefore, it would be necessary either to reduce toxic metals from the Mangla Lake or to control the discharges of untreated urban/industrial wastes, agricultural runoffs and automobile emissions into the Lake.

Acknowledgements

Conflict of interest

The authors have no conflict of interest.

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