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Geochemical speciation, anthropogenic contamination, risk assessment and source identification of selected metals in freshwater sediments—A case study from Mangla Lake, Pakistan

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ABSTRACT

Geochemical speciation of selected metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn) using modified BCR sequential extraction procedure was performed in the sediments collected from Mangla Lake, Pakistan. The extraction method was optimized using certified reference material (BCR-701) which showed significant recoveries (95–106%). Among the metals, Cd, Co, Ni, Pb and Sr exhibited relatively higher mobility and bioavailability, while Cu, Fe, Mn and Zn were found mainly in the residual fractions. Principal component analysis (PCA) revealed four groups of the metals in the sediments; I (Cd–Cr–Ni–Sr), II (Co–Pb), III (Fe–Zn), and IV (Mn–Cu); first two groups were mostly contributed by anthropogenic sources. The pollution indicators (individual contamination factor, enrichment factor and geoaccumulation index) revealed significant anthropogenic contamination of Cd, Co, Ni, Pb, Sr and Zn in the sediments. Risk assessment code (RAC) indicated medium risk for Co and Ni; high risk for Cd and Pb; and very high risk for Sr in the sediments. Cluster analysis (CA) and global contamination factor (GCF) were used to identify the pollution hotspots, which indicated more severe metal contamination at sites near to Mirpur city and other urban/semi-urban areas (S3–S5), especially for Cd, Co, Ni, Pb and Sr.

1. Introduction

Investigations pertaining to the metals in sediments have enlarged in recent years; while previously sediments were only considered as pollutant reservoirs (Passos et al., 2010; Nguyen et al., 2009). A minor fraction (about 1%) of these pollutants remains dissolved in water whereas overwhelming concentrations (99%) are stored in sediments. Therefore, sediments are the major sinks and carriers for contaminants in aquatic environments as some pollutants may be recycled through biological and chemical processes within the water column (Nemati et al., 2011a; Vink, 2009; Bartoli et al., 2011). The metals pollution of sediments is of major concern because of their toxicity, persistence and bio-accumulative nature and may be transferred to the overlying water and thereby entering into the food chain (Nemati et al., 2011a; Díaz-de Alba et al., 2011). In the absence of anthropogenic intrusions, trace metals in sediments are mainly associated with silicates and primary minerals and therefore have limited mobility. However, the metals introduced by human activities show greater mobility and are associated

with other sediment phases, such as, carbonates, oxides, hydroxides and sulfides (Passos et al., 2010; Heltai et al., 2005). Major sources of metals in aquatic systems are the rock weathering and anthropogenic activities including industrial wastewater, drainage of land, atmospheric inputs, soil erosion, biological activities and urban wastes (Díaz-de Alba et al., 2011; Carman et al., 2007).

Estimation of the total metal concentrations in sediments is not suitable to determine their mobility (Tüzen, 2003). The bioavailability and prospective toxicity of the metals to the biota depends on their chemical forms (Ahlf et al., 2009; Arnason and Fletcher, 2003). Therefore, researchers are interested in determining associations of the metals with different geochemical phases (Rauret, 1998). Though sequential extraction procedure is complicated and lengthy, it provides adequate information related to the origin, occurrence, biological/physicochemical aspects, mobilization and transport of metals (Passos et al., 2010). It emulates mobilization and retention of the metals in the aquatic ecosystems by changes such as, pH, redox potential and degradation of organic matter (Tessier et al., 1979; Förstner, 1985). Metals bound in different geochemical fractions are extracted by various reagents such as, inert electrolytes, weak acids, reducing/oxidizing agents and strong mineral acids in a sequence of increasing their extraction strengths (Passos et al., 2010). Various procedures reported in the literature

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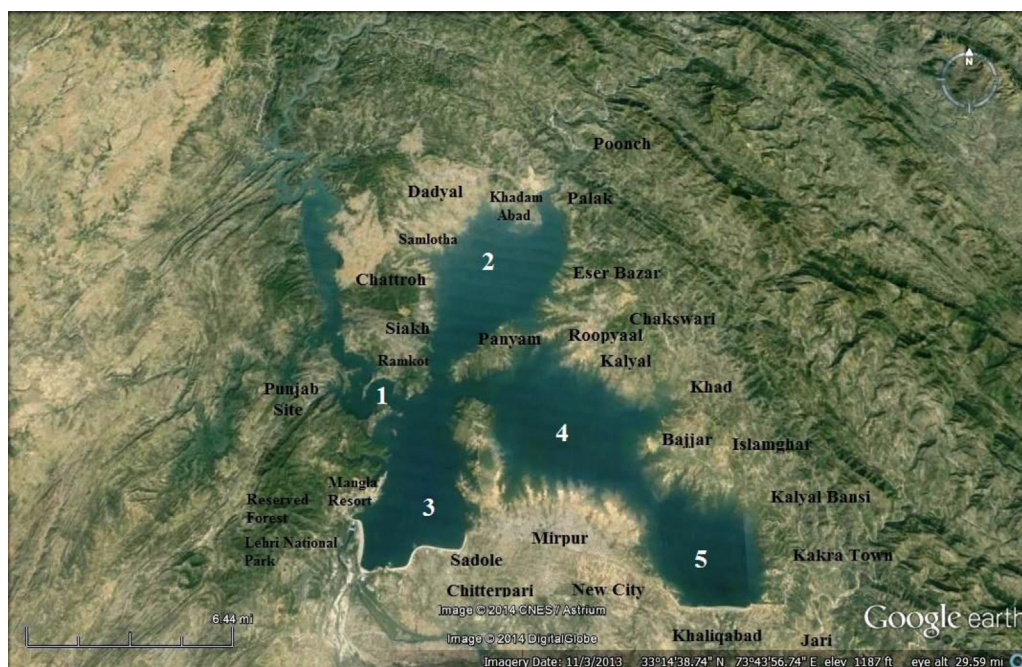*E-mail addresses:* mhshahg@qau.edu.pk, munir_qau@yahoo.com (M.H. Shah).

Fig. 1. Map of the study area showing sampling sites (1–5)

were standardized by European Community Bureau of Reference (BCR) in a multi-step modified sequential extraction procedure, which provides acid extractable, reducible, oxidiseable and residual/immobile fractions of metals in the sediments (Razic and Dogo, 2010; Saracoglu et al., 2009; Ure et al., 1993). This method helps in indication about the mobility, biological availability and potential risks related to the metals contents in the aquatic ecosystems (Passos et al., 2010).

The main objective of the present study was to investigate the distributions of the selected metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn) in different geochemical fractions of the sediments from Mangla Lake, Pakistan, using the optimized three-stage mBCR extraction method. Different pollution indices (RAC, ICF, GCF, EF and I_{geo}) were used in order to determine the contamination and risks associated with the metals in the sediments. Multivariate principal component and cluster analyses were also applied to the results in order to explore the associations between the metals/sites and their major contributing sources in the study area.

2. Material and methods

2.1. Sampling site

Mangla reservoir is one of the largest freshwater resources in Pakistan (Fig. 1). It was impounded in 1967 by damming the River Jhelum near Mirpur city, primarily for storing the water for irrigation and generation of hydroelectric power. Currently water is also used for drinking and household purposes in adjoining areas. The reservoir is fed by two perennial rivers (Jhelum and Poonch) and two non-perennial rivers (Kanshi and Khad). Reservoir being at the junction of these rivers has a square shape with its narrow flanks extending into the river valleys. The average water surface of the lake is approximately 26,500 ha and is divided into five sub-basins commonly referred as pockets, namely, Main Mangla, Jhelum, Poonch, Khad and Jari. The catchments areas of the reservoir are erosion prone resulting into high sedimentation rates in the reservoir thereby continuously reducing its storage capacity (Saleem et al., 2013).

2.2. Sample collection and storage

Surface sediment samples were collected from five major sites (S1 – 33°12′ N, 73°38′E; S2 – 33°17′ N, 73°42′E; S3 – 33°09′ N, 73°40′E; S4 – 33°11′ N, 73°45′E and S5 – 33°08′ N, 73°50′E) of Mangla Lake, Pakistan in winter 2012. A total of 80 composite surface sediments samples (1–15 cm, top layer) were collected in pre-cleaned Ziploc polythene bags using a snapper (Φ 5 cm). Each composite sample was composed of 5–7 sub-samples collected within an area of 20–30 m^2. The samples were kept in plastic ice-cold containers. Large objects including stones, pieces of brick, concrete and cinders were manually removed. The sediment samples were oven dried, grounded, homogenized, sieved through a 2 mm mesh and sealed in clean polythene bags and then stored in a refrigerator until further processing (Nemati et al., 2011a; Kannan et al., 2008). Every precaution was taken to avoid contamination during sampling, drying, grinding, sieving and storage.

2.3. Reagents and glassware

All reagents used were of analytical grade (certified purity >99.9%) procured from E-Merck, Germany or BDH, UK. Deionized water was used for the preparation of working standards at the time of analysis by successive dilution of the standard metal solutions (1000 mg/L). All laboratory glassware (Pyrex) was cleaned using a HNO_3 (20%, v/v) bath overnight, followed by repeated rinsing with doubly distilled water (Díaz-de Alba et al., 2011). For the removal of adherent organic impurities from glassware, they were rinsed with acetone. Finally the glassware was dried in an electric oven maintained at 80 °C for about eight hours prior to use.

2.4. Physicochemical characterization

Sediment samples were air-dried and sieved through a 2 mm sieve. Electrical conductivity (EC) and pH were measured with a multimeter (Bench Meter, Martini Instrument Mi 180) in a 1:2 sediment:water suspension (Radojevic and Bashkin, 1999). Organic matter content (OM) was estimated by measuring the loss of weight on ignition at 550 °C (Díaz-de Alba et al., 2011).

2.5. Pseudo total metal digestion

Pseudo total metal concentrations were determined by digesting 1–2 g dried sediment in a microwave system using a freshly prepared acid mixture of 9 mL HNO_3 and 3 mL HCl (US-EPA, 2007). A reagent blank was also prepared with the same amount of acids without the sediment sample. The digests were then filtered through the fine filters (0.45 µm, pore size) and made up to 50 mL with deionized water and stored at 4 °C until metal analysis.

2.6. Sequential extraction procedure

Sequential extractions were performed using a three-stage modified BCR procedure plus the residual fraction (Passos et al., 2010; Nemati et al., 2011a). This modified procedure proposed and validated by the BCR (Community Bureau of Reference) is considerably more acceptable as the standard method by many laboratories (Pueyo et al., 2008; Nemati et al., 2011b). Furthermore, standard reference materials provision (i.e., BCR-701, BCR-601 and BCR-483) makes this method more useful for various laboratories, in terms of method validation and quality control. Consequently, the method is a good option for soils/sediments analysis and analytical data obtained by application of the method have been used to envisage metal mobility in soils/sediments (Pueyo et al., 2008; Nemati et al., 2011b; Razic and Dogo, 2010). A briefed description of this procedure is provided below:

Stage 1 (acid extractable/exchangeable fraction, F1): 40 mL 0.11 M acetic acid solution was added to 1.0 g of sample, with agitation for 16 h at room temperature in an auto-shaker operating at 320 rotations per minute. The extract was separated from the solid phase by centrifugation at 3000 rpm for 20 min and the supernatant separated by decantation was stored for afterward analysis. The residue was washed with 20 mL of deionized water by shaking for 20 min on an auto-shaker and centrifuged for 20 min at 3000 rpm. Subsequently, the supernatant was decanted.

Stage 2 (easily reducible fraction, F2): 40 mL of a 0.5 M hydroxylammonium chloride solution (pH 1.5) was added to the residue from Stage 1, with agitation for 16 h at room temperature in an auto-shaker operating at 320 rotations per minute. The separation of the extract, collection of the supernatant and rinsing of residues were the same as described in Stage 1.

Stage 3 (oxidiseable fraction, F3): 10 mL of 8.8 M H_2O_2 solution (pH 2–3) was added to the Stage 2 residue. The vessel was loosely covered to prevent substantial loss of hydrogen peroxide and left at room temperature for 1 hour with occasional manual shaking. It was then heated to 85 ± 2 °C for 1 h in a water bath, until the volume was reduced to 2–3 mL. Another 10 mL portion of 8.8 M H_2O_2 solution was added and the mixture was heated to dryness at 85 ± 2 °C for 1 h. After cooling, 50 mL of 1.0 M ammonium acetate solution (pH 2) was added to the residue, with subsequent agitation for 16 h at room temperature in an auto-shaker operating at 320 rotations per minute. The extract was separated from the solid phase by centrifugation, as above. Reagent blanks were also prepared with the same amount of the reagents without sediment sample.

Stage 4 (residual fraction, F4): 10 mL of freshly prepared aqua-regia solution was added to the stage 3 residue, drop by drop to reduce foaming. The vessel was allowed to proceed for 16 h at room temperature for slow dissolution of the residual sediment and then heated slowly to reflux conditions which were maintained for 2 hours. After cooling the digests were filtered through the fine filter paper into 50 mL volumetric flasks. The insoluble residue onto the filter paper was washed with a 0.5 M HNO_3 and the final volume (50 mL) were adjusted with 0.5 M HNO_3.

2.7. Determination of metal concentrations

Metal concentrations in the digests acquired at each stage were determined using a flame atomic absorption spectrometer (Shimadzu AA-670, Japan). Calibration line method was used for the quantification of selected metals and the digests were appropriately diluted whenever required (Radojevic and Bashkin, 1999). All the measurements were made in triplicate. Instrument settings were as recommended in the manufacturer's manual, with wavelengths (nm) of 228.8 (Cd), 240.7 (Co), 357.9 (Cr), 324.8 (Cu), 248.3 (Fe), 279.5 (Mn), 232.0 (Ni), 217.0 (Pb), 460.7 (Sr) and 213.9 (Zn).

2.8. Determination of method efficiency

Reliability and quality of pseudo-total metal analysis was evaluated by analysis of three replicates of standard reference material SRM-2709, whereas efficiency of the sequential extraction method was evaluated by analysis of three replicates of certified sediment reference material (BCR-701, European Community Bureau of Reference). For each extraction step, the concentration of every metal was compared with the reference value and the recovery was calculated as follows:

$$\text{Recovery}(\%) = \left(\frac{\text{Measure d Value}}{\text{Certified Value}} \right) \times 100 \tag{1}$$

Moreover, the reagent blanks were also prepared during pseudo-total metal digestion and sequential extractions in the same manner to avoid cross contamination and to ensure reliability of the metal analysis. An internal check on the sequential extraction method was performed by comparing the total amount of metal extracted by different reagents using sequential extraction procedure with the results of the pseudo total metal concentration (Nemati et al., 2011a). The recovery of the sequential extraction method was calculated as follows:

$$\text{Recovery}(\%) \left(\frac{C_{ex} + C_{red} + C_{ox} + C_{res}}{C_{pseudototal}} \times 100 \right) \tag{2}$$

2.9. Statistical analyses

Multivariate statistical analysis has been widely applied in environmental studies, which provide an effective way to reveal the relationships between multiple variables and thus they are helpful for the understanding of the influencing factors as well as sources of the chemical components (Zhang et al., 2008; Uría et al., 2009). The multivariate principal component analysis (PCA) was performed using varimax-normalized rotation on the analytical data to evaluate the sources/origins of the variables. PCA mainly reduces the dimensionality of the variables and amalgamates the most of the variables with lesser factors that explain the major variations within the data. Each factor is a weighted and linear combination of the original variables. Cluster analysis (CA) was performed using Ward's method and the results were reported in the form of dendrogram. CA organizes a set of variables into two or more mutually exclusive unknown groups/clusters based on combination of internal variables (Iqbal and Shah, 2011). PCA/CA analyses were performed by using STATISTICA software (StatSoft, 1999).

2.10. Risk assessment code (RAC)

The binding strength of metals in various geochemical phases establishes their bio-availability and their associated risks in aquatic ecosystems. Risk assessment code (RAC) was computed based on the bioavailable metal concentrations in terms of percent contribution in first geochemical fraction (F1) in mBCR procedure, where the metals are softly bound to the solid phases and cause a great risk to organisms (Jain and Ran, 2004). The risk code may

Table 1
Statistical summary of physicochemical parameters (mean, range) in the sediments at different sites.

Code	pH	EC (µS/cm)	OM (%)
S-1	7.68, 7.54–7.92	329.5, 201.8–442	6.37, 4.50–8.59
S-2	7.73, 7.43–8.05	345.6, 241.9–466.3	7.33, 5.37–9.37
S-3	7.92, 7.74–8.08	196, 167.4–231.9	4.82, 3.20–7.90
S-4	7.86, 7.63–8.10	324.2, 232.9–485.9	6.46, 5.08–7.79
S-5	7.79, 7.58–8.10	292.7, 230.2–491.7	5.73, 3.90–8.87

Table 2
Metal concentrations (mg/kg) in the sediments by mBCR sequential extraction method.

		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn
S-1	Exchangeable	0.578	13.24	0.913	2.330	40.25	87.24	5.505	8.071	122.3	3.076
	Reducible	0.017	6.651	3.339	4.997	2684	77.32	12.61	9.718	9.752	12.53
	Oxidiseable	0.320	4.286	0.152	1.445	198.7	10.43	20.54	2.421	2.818	1.002
	Residual	0.698	13.80	13.48	8.483	2335	174.8	32.76	1.518	13.16	102.9
	Total fractions	1.612	37.98	17.88	17.26	5258	349.8	71.41	21.73	148.0	119.5
	Pseudo total	1.637	36.66	18.45	17.43	5216	350.4	69.61	21.86	149.7	115.7
	Recovery (%)	98.48	103.6	96.92	99.02	100.8	99.84	102.6	99.39	98.88	103.3
	ICF	1.310	1.750	0.327	1.034	1.252	1.001	1.180	13.32	10.25	0.161
	RAC (%)	35.85	34.86	5.103	13.51	0.765	24.94	7.708	37.15	82.62	2.573
S-2	Exchangeable	1.407	12.77	0.510	2.888	45.85	89.13	8.528	9.773	108.0	2.045
	Reducible	0.601	7.320	4.010	3.273	1431	61.01	11.08	5.336	11.50	9.497
	Oxidiseable	0.648	3.087	1.769	0.997	141.9	11.91	18.10	0.174	3.036	1.590
	Residual	0.567	11.59	14.60	16.91	1983	227.8	31.48	5.582	14.54	107.7
	Total fractions	3.223	34.76	20.89	24.06	3603	389.9	69.19	20.87	137.1	120.8
	Pseudo total	3.251	34.35	21.91	24.52	3639	385.1	68.80	21.34	138.3	124.1
	Recovery (%)	99.18	101.2	95.34	98.13	99.00	101.3	100.6	97.75	99.08	97.37
	ICF	4.685	1.999	0.431	0.423	0.816	0.711	1.198	2.738	8.427	0.122
	RAC (%)	43.66	36.72	2.440	12.00	1.273	22.86	12.33	46.84	78.79	1.693
S-3	Exchangeable	1.300	10.26	1.749	2.311	55.40	69.57	16.28	15.26	74.15	1.406
	Reducible	1.074	14.84	4.897	2.985	2474	97.20	10.83	9.708	9.367	14.05
	Oxidiseable	1.112	4.774	2.998	1.312	128.7	11.76	20.98	3.998	9.870	1.362
	Residual	0.637	14.75	16.13	19.36	2291	233.5	35.92	6.656	14.75	115.1
	Total fractions	4.122	44.62	25.78	25.96	4950	412.0	84.01	35.62	108.2	131.9
	Pseudo total	4.061	45.18	25.91	25.35	5039	415.4	85.85	35.56	109.3	133.2
	Recovery (%)	101.5	98.76	99.46	102.4	98.22	99.18	97.86	100.2	98.98	99.06
	ICF	5.471	2.025	0.598	0.341	1.160	0.765	1.339	4.352	6.330	0.146
	RAC (%)	31.52	22.99	6.785	8.900	1.119	16.89	19.37	42.84	68.57	1.066
S-4	Exchangeable	0.749	7.387	1.199	2.608	42.47	83.92	11.46	14.22	144.1	1.772
	Reducible	0.487	11.30	5.393	3.246	3459	91.06	8.975	20.43	25.59	16.34
	Oxidiseable	1.199	5.168	3.384	0.537	156.9	10.09	11.22	5.094	19.36	1.822
	Residual	4.317	19.61	19.37	16.78	2259	268.2	36.14	7.602	12.06	131.8
	Total fractions	6.751	43.46	29.35	23.17	5918	453.2	67.78	47.34	201.1	151.8
	Pseudo total	6.758	44.11	29.50	23.50	5955	438.4	68.31	47.97	196.9	154.8
	Recovery (%)	99.91	98.57	99.50	98.62	99.38	103.4	99.23	98.66	102.1	98.03
	ICF	0.564	1.216	0.515	0.381	1.619	0.690	0.876	5.228	15.68	0.151
	RAC (%)	11.09	16.20	4.085	11.25	0.718	18.52	16.90	30.03	71.65	1.168
S-5	Exchangeable	2.346	5.041	2.358	2.184	19.41	88.83	9.767	9.894	176.8	0.095
	Reducible	1.410	22.30	3.731	3.107	2396	77.61	10.68	9.185	46.72	11.38
	Oxidiseable	1.050	3.556	4.517	0.512	157.1	12.57	18.27	4.905	9.197	4.217
	Residual	1.276	15.72	19.20	16.55	2279	294.4	22.19	2.715	18.17	89.78
	Total Fractions	6.081	46.62	29.81	22.35	4852	473.4	60.90	26.70	250.9	105.5
	Pseudo total	6.248	45.48	29.27	22.23	4943	466.4	61.65	26.91	254.8	108.6
	Recovery (%)	97.32	102.5	101.8	100.5	98.17	101.5	98.78	99.21	98.46	97.16
	ICF	3.768	1.965	0.552	0.351	1.129	0.608	1.745	8.835	12.81	0.175
	RAC (%)	38.58	10.82	7.911	9.772	0.400	18.77	16.04	37.06	70.47	0.090

be classified as; RAC < 1% indicates no risk to the aquatic system, RAC = 1–10% reflects low risk, RAC = 11–30% shows medium risk, RAC = 31–50% indicates high risk and RAC > 50 reflects that the sediments may pose a very high risk, with the metals easily able to enter the food chain (Nemati et al., 2011a; Jain and Ran, 2004; Perin et al., 1985).

2.11. Individual contamination factor (ICF) and global contamination factor (GCF)

The determination of contamination factor of metals is an important aspect that indicates the degree of risk of a metal to environment in relation with its retention time. The individual contamination factors (ICF) for the different sediment samples were obtained by dividing the sum of the non-residual fractions (F1 + F2 + F3) by the residual fraction (F4) of each sample, while GCF for each site was calculated by summing the ICF of all the metals obtained for the sediment samples (Ikem et al., 2003). The individual contamination factor (ICF) and global contamination factor (GCF) classifications were interpreted as suggested by Zhao et al. (2012): ICF < 0 & GCF < 6 – indicates low, 1 < ICF < 3 & 6 < GCF < 12 – moderate, 3 < ICF < 6 & 12 < GC < 24 – considerable and ICF > 6 & GCF > 24 – high contamination.

2.12. Enrichment factor (EF)

Enrichment factor (EF) estimates the anthropogenic impact on sediments, using a normalization element in order to alleviate the variations produced by heterogeneous sediments. The reference element is selected so as to have minimum variability of occurrence or is present in such large concentrations in the studied environment, that neither small concentration variations nor other synergistic or antagonistic effects towards the examined elements are significant (Iqbal and Shah, 2011; Abrahim and Parker, 2008). Since the sediments from the Lake are rich in Fe content, it was selected as normalization element. In present study, enrichment factors (EF) were calculated by using the following relationship:

$$EF = \frac{[X/Fe]_{sample}}{[X/Fe]_{crust}} \tag{3}$$

where $[X/Fe]_{sample}$ and $[X/Fe]_{crust}$ refer, respectively, to the ratios of arithmetic mean concentrations (mg/kg, dry weight) of the target metal and Fe in the examined sediments and continental earth crust (Lide, 2005). The EF values were interpreted as suggested by Sakan et al. (Sakan et al., 2009): EF < 1 indicates no enrichment, EF 1–3 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.

2.13. Geoaccumulation index (I_{geo})

The index of geoaccumulation (I_{geo}) enables the assessment of contamination by comparing the current and pre-industrial concentrations of the metals in earth crust (Iqbal and Shah, 2011; Muller, 1969). It is computed using the following mathematical formula:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \tag{4}$$

where 'C_n' is the measured concentration of the metal in the sediment samples and 'B_n' is the geochemical background value in earth crust (Lide, 2005). The factor 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to geogenic variations. The I_{geo} values were interpreted as: $I_{geo} \leq 0$ – practically uncontaminated, $0 < I_{geo} < 1$ – uncontaminated to moderately contaminated, $1 < I_{geo} < 2$ – moderately contaminated, $2 < I_{geo} < 3$ – moderately to heavily contaminated, $3 < I_{ge} < 4$ – heavily contaminated, $4 < I_{geo} < 5$ – heavily to extremely contaminated and $5 < I_{geo}$ – extremely contaminated (Muller, 1969).

3. Results and discussion

3.1. Physicochemical characterization

The statistical summary of pH, EC and OM in sediments at various sites is described in Table 1. The pH and EC values ranged from 7.43–8.10 and 167.4 to 491.7 μS/cm with mean values of 7.79 and 297.6 μS/cm, respectively. The organic matter contents ranged from 3.20 to 9.37%, with a mean value of 6.14%, obtaining the highest percentages in sediments from site 4 and 2. The studied sediments contained high organic matter contents that could decrease the metal availability by complexing. Association of the metals with OM can be explained by the high affinity of the metals for the humic substances that comprise much of this material. This is due to the formation of the stable metal complexes and insoluble metal sulfides that are important sinks for trace metals in the sediments (Passos et al., 2010).

Table 3
Pseudo total concentration of metals (mg/kg) in the sediments at different sites.

Location	Metal concentration
S-1	Fe > Mn > Sr > Zn > Ni > Co > Pb > Cr > Cu > Cd
S-2	Fe > Mn > Sr > Zn > Ni > Co > Cu > Cr > Pb > Cd
S-3	Fe > Mn > Zn > Sr > Ni > Co > Pb > Cr > Cu > Cd
S-4	Fe > Mn > Sr > Zn > Ni > Pb > Co > Cr > Cu > Cd
S-5	Fe > Mn > Sr > Zn > N > Co > Cr > Pb > Cu > Cd

3.2. Pseudo total metal concentrations

The concentrations of selected metals at five major sampling sites are listed in Table 2 and the comparative results of pseudo-total metal concentrations are presented in Table 3. Among the metals, Fe and Mn were found to be the dominant metals, followed by Sr and Zn while Cr, Cu and Cd concentrations were the lowest. Moreover, Ni, Co and Pb levels were noticeably high at all the sites. The highest amounts of Cd, Cr, Fe, Pb and Zn were obtained at site S4, while the highest amounts for Co, Mn and Sr were obtained at site S5. Furthermore the highest concentrations of Cu and Ni were found at S3. Overall, the highest concentrations of toxic metals were found at that sites which are attached with Mirpur city (S3–S5) and also there is a main heavy traffic road on the bank of the Lake. High concentrations of Co could be due to oil and petrol products discharged by shipping and boating activities in the Lake (Bartoli et al., 2011). Similarly higher levels of Cd, Ni and Pb could be due to industrial and municipal activities, dumping and roadside run-offs and automobile exhaust (Li et al., 2007).

3.3. Sequential extraction results

The metal concentrations in surface sediments from each extraction step are shown in Table 2. The discussion on the distribution patterns of the metals was divided into four groups depending on the degree of their association with the different phases: Cr, Cu, Mn, Ni and Zn were found to be present mainly in the residual fraction; Cd and Co were predominantly found in the exchangeable, reducible and residual fractions; Sr and Pb were found in the exchangeable fraction, but Pb was also found in the easily reducible fractions; and large amounts of Fe were obtained in reducible and residual fractions.

In this study, the results as illustrated in Fig. 2 showed that higher concentrations were found in the residual fraction for Cr (62–75%), Mn (49–62%), Ni (36–53%), Cu (49–74%), and Zn (85–89%). These findings are similar to the results reported by Díaz-de Alba et al. (2011) and Yuan et al. (2004). Elevated concentrations of the metals in the residual fraction indicated that sediments were relatively unpolluted and that the metals were derived mainly from geogenic origin (Davutluoglu et al., 2010). In the residual fraction, metals are bound to silicates and are therefore unavailable to the aquatic system (Tüzen, 2003). Anthropogenic metals are predominantly found in the most labile sediment fractions, which are vulnerable to small changes in environmental conditions, such as those caused by human activity (Alves et al., 2007). The phase distribution of Cr in this study indicated that Cr was mostly retained in the residual fraction similar to the results reported by Passos et al. (2010). Less than 8%, 20% and 16% of Cr have been found in exchangeable (F1), easily reducible (F2) and oxidiseable (F3) fractions, respectively. However, the amount of Cr in fractions 1–3 was less than 37% at all stations indicating the pedogenic source of Cr. Furthermore, Cr showed the highest portion in residual fraction (75%) at S1 and noticeable concentration in reducible fraction at S2–S4 too.

The highest portion of Cu was obtained in residual fraction and less than 15% of Cu had been found in each other fraction at all
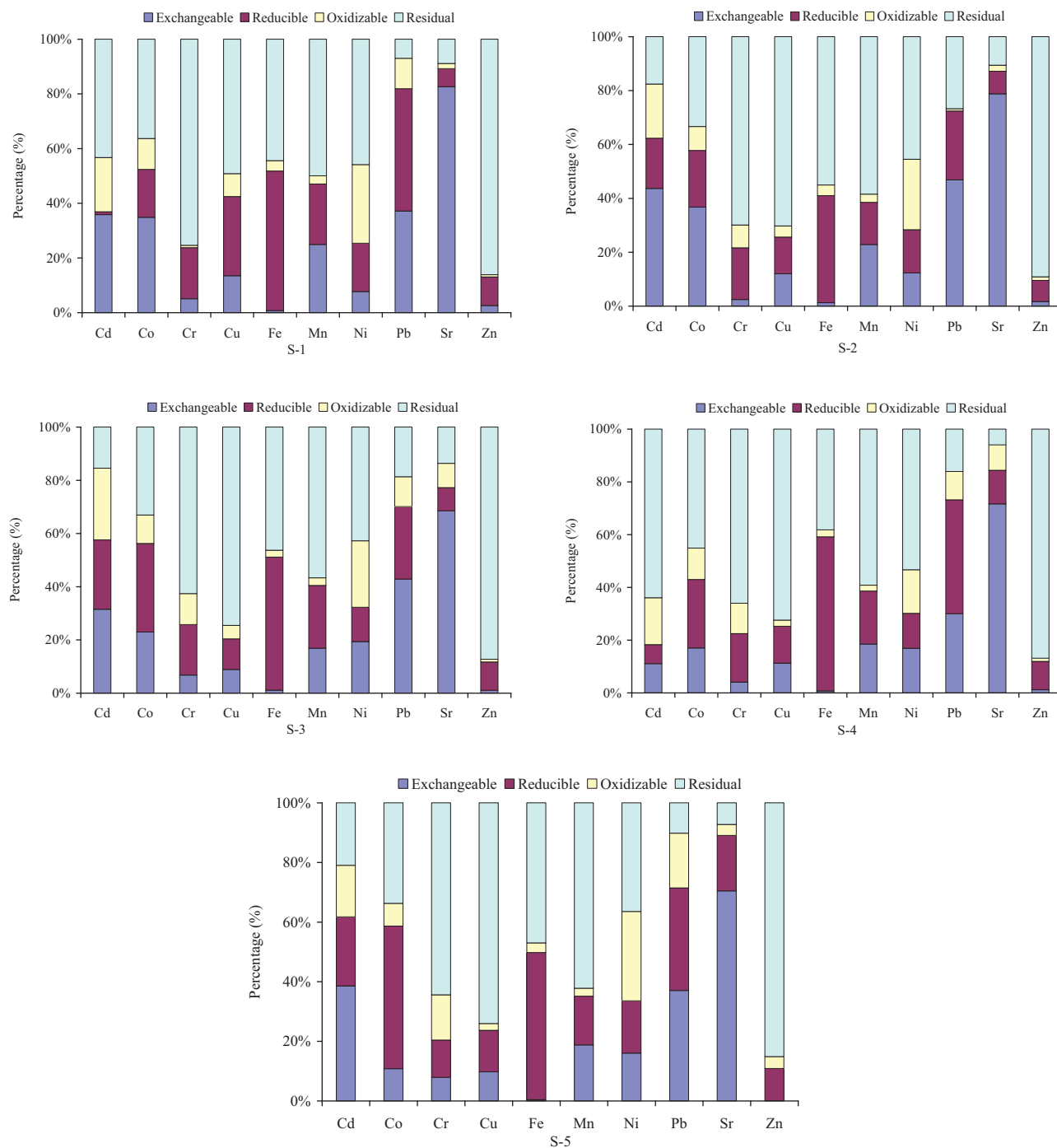
Fig. 2. The average percentage of metal fractionation in the sediments at different sites.

sites expect S1 where 29% Cu was obtained in reducible fraction. The highest concentration of Cu was found in residual at S3. The dominant portion of Mn (>50%) was in residual fraction while less than 25%, 24% and 4% of Mn had been found in exchangeable, easily reducible and oxidiseable fractions, respectively at S1–S5. The lower percentage of Mn in organic fraction probably results from the competition between Fe–Mn-organic complex and hydrous Fe–Mn oxide forms (Sundaray et al., 2011). The proportion of Ni concentration (about 36–53%) was highest in the residual fraction and its noticeable amount (about 20–30%) was found in the oxidiseable fraction. However, Ni showed less than 35% of total contents in fractions 1 and 2. The dominant portion of Zn concen-

tration (85–89%) was in residual fraction while less than 3%, 11% and 4% of Zn have been found in exchangeable, easily reducible and oxidiseable fractions, respectively. Elements associated with the residual fraction are likely to be incorporated in aluminosilicate minerals and so are unlikely to be released to pore-waters through dissociation (Tüzen, 2003).

Among the selected metals, Co and Cd were distributed in all four fractions of the sediment phases. The maximum Co concentration (>33%) was found in residual fraction at all sites with the exception of S2 & S5 where its highest portion was in exchangeable and reducible fractions, respectively. Elevated concentrations of Co could be due to activities such as fishing/boating activities

and shipping industries (Nemati et al., 2011a) which could be the probable source of contamination in the area.

The levels of Cd in sediments have been the focus of much concern due to its high toxicity because it has been reported as one of the most labile metals (Marmolejo-Rodrıguez et al., 2007). In this study, Cd was found to be the mobile metal as its high portion (30–50%) was in exchangeable fraction at all sites except S4. The results were in agreement with the fact that Cd has been reported as being among the most labile metal in the reported literature (Díaz-de Alba et al., 2011; Marmolejo-Rodrıguez et al., 2007). The concentration of Cd was found relatively higher in the residual fraction at S1 and S4, whereas noticeable portion of Cd (17–26%) was found in oxidisable fraction at sites S1–S5. It was contributed by untreated domestic waste, roadside run offs, agricultural and industrial activities in the study area (Li et al., 2007).

The maximum portion of Pb was found in exchangeable and easily reducible fractions at all sites. The concentration of Pb was the maximum in exchangeable fraction at S2, S3 and S5 showing great mobility and toxicity, while in reducible fraction (iron–manganese oxide fraction) at S1and S4 showing anthropogenic intrusions (Zhao et al., 2012). The higher percentage of Sr was obtained in exchangeable fraction (69–83%) while less than 19%, 10% and 14% in easily reducible, oxidiseable, and residual fractions, respectively at S1–S5. Strontium might be contributed by excavation activities carrying out in the up-raising areas of the Lake as Sr is known to have geochemical resemblance with Ca in lime stones (Kelepertzis, 2014). The freshwater lakes are strongly influenced by intensive human activities and Pb is mainly derived from industry and municipal activities, atmospheric inputs and automobile exhaust (Li et al., 2007). Automobile exhaust, municipal wastes and industrial activities in the area might be the major source of Pb in the sediments.

Higher percentage of Fe was obtained in both reducible and residual fractions while less than 4% in exchangeable and oxidiseable fractions at all sites. Among the non-lithogenic fractions, Fe–Mn oxy-hydroxide is the main scavenger for all metals (except Cu and Cd). This attributes to the adsorption, flocculation and co precipitation of the metals with the colloids of Fe and Mn oxy-hydroxide (Passos et al., 2010; Rath et al., 2009). The lower percentage of Fe in organic fraction (oxidiseable) probably due to the competition with Mn organic complex and hydrous Fe–Mn oxide forms (Sundaray et al., 2011).

3.4. Internal check recovery

An internal check on the results of the sequential extraction method was performed and the sums of the four fractions were in good agreement with the pseudo total digestion results at all sites, with acceptable recoveries (96–104%) as shown in Table 4. Thus the mBCR sequential extraction procedure was found reliable and reproducible. The results obtained using aqua-regia digestion method were also evaluated by the analysis of SRM 2709, which exhibited good accuracy of analysis (97–102%), Table 4.

Table 4
Recoveries of standard sediment reference material BCR-701 by applying mBCR sequential extraction method and SRM 2709 by aqua regia digestion method ($n = 3$).

Metal	BCR 2709, recovery (%)				SRM 2709
	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Recovery (%)
Cd	102 ± 4	104 ± 3	103 ± 7	105 ± 3	97 ± 4
Co	–	–	–	–	99 ± 2
Cr	106 ± 6	99 ± 4	96 ± 3	99 ± 3	102 ± 2
Cu	97 ± 6	98 ± 5	104 ± 5	103 ± 4	101 ± 3
Fe	–	–	–	–	98 ± 3
Mn	–	–	–	–	99 ± 2
Ni	101 ± 4	95 ± 5	102 ± 3	105 ± 4	102 ± 3
Pb	102 ± 6	98 ± 4	103 ± 6	104 ± 5	97 ± 4
Sr	–	–	–	–	98 ± 4
Zn	96 ± 3	102 ± 3	101 ± 8	100 ± 2	98 ± 3

3.5. Comparison of the metal levels with reported studies

The average metal levels in sediments were compared with the reported studies form other regions around the world as given in Table 5. Mean levels of Cr and Cu were found to be lower than most of the reported levels in Table 5 except Rawal Lake, Pakistan (Iqbal et al., 2013) and Poxim River Estuary, Brazil (Passos et al., 2010), whereas, the present Fe levels were found to be higher than those reported for Khanpur Lake, Pakistan (Iqbal and Shah, 2014). Average levels of Mn were higher than the reported levels for Rawal Lake and Khanpur Lake, Pakistan (Iqbal et al., 2013; Iqbal and Shah, 2014), but significantly lower than the reported concentrations for Mahanadi River, India (Sundaray et al., 2011) and Algeciras Bay Spain (Díaz-de Alba et al., 2011). Zinc concentrations were found higher than the levels reported in most of the studies except Mahanadi River, India (Sundaray et al., 2011). Average levels of Pb in the present study were relatively higher than those reported by most of the investigations apart from Mahanadi River, India (Sundaray et al., 2011) and Sungai Buloh, Malaysia (Nemati et al., 2011a). The measured average concentrations of Cd, Co, Ni and Sr were considerably higher than the reported levels in Table 5.

3.6. Source apportionment

Metal concentrations and organic matter contents in the sediments were further investigated by PCA to find out their associations and possible metal sources. The resulting principal component loadings are explicated in Table 6. Four principal components (PC) were obtained with eigen value greater than 1, explaining cumulative variance of 75.13%. PC1 showed elevated loadings for Cd, Cr, Ni and Sr; while PC2 exhibited dominant loadings of Cd, Co, Pb and OM. These groupings pointed out similarities among these metals/organic matter, indicating that the metals could be contributed by anthropogenic sources. PC3 and PC4 exhibited significant loadings in favor of Fe–Zn and Cu–Mn, respectively, signifying that these metals might be attributed to the lithogenic sources.

Cluster analysis (CA) was applied on standardized data-sets sorted by sampling sites to understand the similarities among them

Table 5
Average metal concentrations (mg/kg, dry weight) measured in the present study in comparison with other reported studies.

Location	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Zn	Reference
Mangla Lake, Pakistan	4.391	41.16	25.01	22.61	4959	411.1	70.84	30.73	169.8	127.3	Present Study
Rawal Lake, Pakistan	2.130	3.901	12.15	7.155	14,979	306.4	–	16.94	114.0	18.18	Iqbal et al. (2013)
Khanpur Lake, Pakistan (Summer)	1.883	–	34.66	36.84	447.5	–	33.71	–	86.09		Iqbal and Shah, (2014)
Khanpur Lake, Pakistan (Winter)	2.457	–	37.65	28.05	3,791	321.4	–	18.24	–	61.90	
Mahanadi River, India	4.2	–	72	36	60000	1133	55	131	–	137	Sundaray et al. (2011)
Algeciras Bay Spain	0.3	11	112	17	28129	534	65	24	–	73	Díaz-de Alba et al. (2011)
Poxim River Estuary, Brazil	0.23	–	7.98	8.79	–	–	1.71	12.04	–	19.02	Passos et al. (2010)
Sungai Buloh, Malaysia	0.316	4.01	39.51	34.73	–	–	16.99	37.27	–	93.98	Nemati et al. (2011a)

Table 6
Principal component loadings[a] of selected metals in the sediments.

	PC 1	PC 2	PC 3	PC 4
Eigen value	3.033	2.268	1.937	1.026
% Total variance	27.58	20.62	17.61	9.324
% Cumulative variance	27.58	48.19	65.80	75.13
Cd	0.697	0.375	–	–
Co	–	0.842	–	–
Cr	0.661	–	0.423	–
Cu	–	–	0.343	0.604
Fe	–	–	0.807	–
Mn	–	–	–	0.933
Ni	0.862	–	–	–
Pb	–	0.814	–	–
Sr	0.723	–	–	0.266
Zn	–	–	0.798	–
OM	–	0.746	–	–

[a]PC loadings < 0.250 are omitted
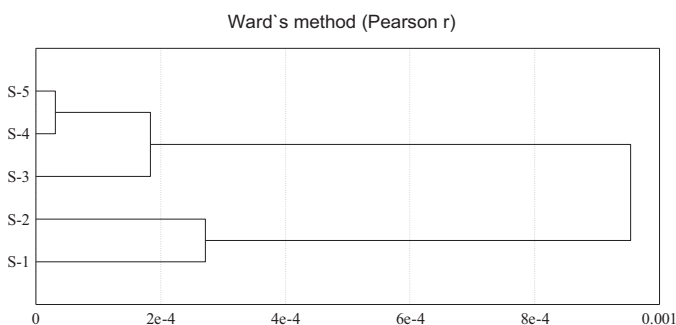
Fig. 3. Description of cluster analysis for different sites.

Table 7
Comparison of risk assessment code values (RAC, %) at different sites.

	S-1	S-2	S-3	S-4	S-5
Cd	H	H	H	M	H
Co	H	H	M	M	M
Cr	L	L	L	L	L
Cu	M	M	L	M	L
Fe	N	L	L	N	N
Mn	M	M	M	M	M
Ni	L	M	M	M	M
Pb	H	H	H	H	H
Sr	VH	VH	VH	VH	VH
Zn	L	L	L	L	N

VH: very high; H: high; M-medium; L: low; and N: no risk.

which separated the five locations into two main clusters: I (S3–S5) and II (S1–S2), as shown in Fig. 3. Cluster I sites were distinguished from the rest with high influence of the metal pollution probably due to their position near to urban and the Lake up-raising areas. Relatively less polluted sites showed a mutual cluster.

3.7. The risk assessment code (RAC)

It determines the availability of sedimentary metals by applying a scale to the proportions of the metals in bioavailable fraction. This is imperative because the metal concentrations attributed to anthropogenic activities remain loosely held to sediments as exchangeable fraction (F1) which could be released to aquatic phase and/or could be taken by benthic plants/animals, causing environmental toxicity (Sundaray et al., 2011; Liu et al., 2008). Comparative evaluation of RAC levels (%) in sediments at various sites is given in Table 7. The RAC results manifested no risk for Fe (<1%) except at sites S2–S3 and low risk for Cr at S1–S5 and Zn at S1–S4. Medium risk was indicated by Mn at S1–S5, Ni at S2–S5, Co at S3–S5, Cu at
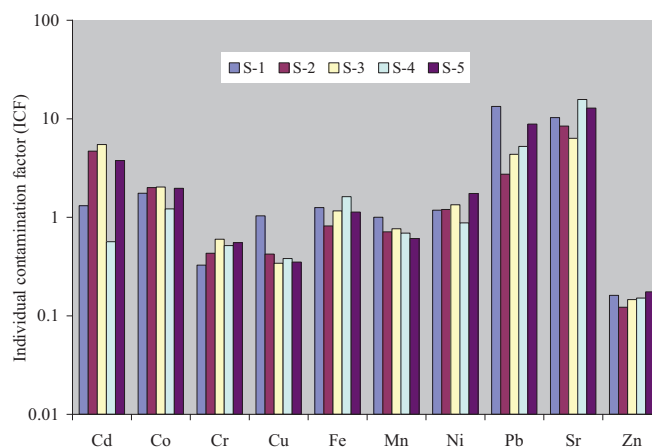
Fig. 4. Comparison of individual contamination factors (ICF) at different sites.

S1, S2 & S4 and Cd at S4. Moreover a high risk was shown by Pb at S1–S5, Cd at S1–S3 & S5, and Co at S1–S2. Strontium manifested a very high risk at all sites and was considered dangerous. Overall, RAC indicated that Cd, Co, Pb and Sr were highly mobile and bioavailable in the aquatic environment. Therefore, a significant remediation must be applied for Sr, Cd, Pb and Co mobilization at the earliest as they might enter in the food chain and pose threat in the study area.

3.8. Individual contamination factor (ICF) and global contamination factor (GCF)

The determination of metal contamination factor is an important aspect that indicates the degree of metals risk to the environment in relation with its retention time. A high contamination factor of the metals shows low retention time and high risk to the environment. The ICF was used to estimate the relative retention time of the metals in sediments. Fig. 4 shows the individual contamination factors of each metal in the surface sediments at various sites. The ICF results showed the highest ability of Cd, Sr and Pb to be released from the Lake to overlying water, whereas Zn, Cr, Cu, Fe and Mn manifested the lowest. Moreover, ICF of Ni and Co was also significant at all sites. The residual concentration of any metal is considered a non-mobile fraction and is an important part in influencing the mobility nature of the metal. The combined high concentration effect of metals, such as, Cd, Sr and Pb at sites S3–S5 with high potential mobility demonstrated the increased possible risk of these metals to the surrounding environment and aquatic biota. The highest ICF factors for Cd, Sr and Pb were found in the sediments near semi-urban and urban areas; Khaliqabad, Islamgarh, Mirpur City and New City (Fig. 1). Though GCF results revealed considerable to high risks to the surrounded environment at all sites, but the degree of contamination was relatively higher in sediments from sites S3-S5.

3.9. Enrichment factor (EF)

The geochemical normalization has been used to obtain enrichment factor and to assess anthropogenic contributions of the metals in sediments (Zhao et al., 2012; Rath et al., 2009). Average enrichment factors of the metals in the acid-extract of the sediments from various sites are shown in Fig. 5. The EF values for Cr (EF = 2–3) indicated minor-moderate enrichment, Cu (EF = 3–6), Sr (EF = 3–8) and Mn (EF = 4–6) showed moderate-moderately severe enrichment, and EF values of Ni (EF = 8–13) manifested moderately severe-severe enrichment. Among the selected metals, Zn (EF = 18–25) and Co (EF = 16–21) showed severe enrichment;
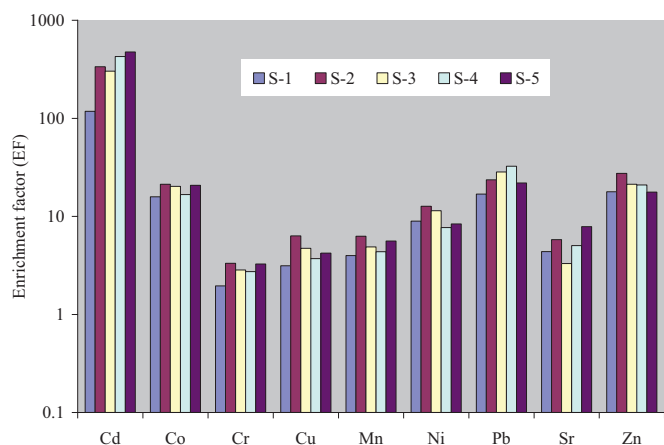
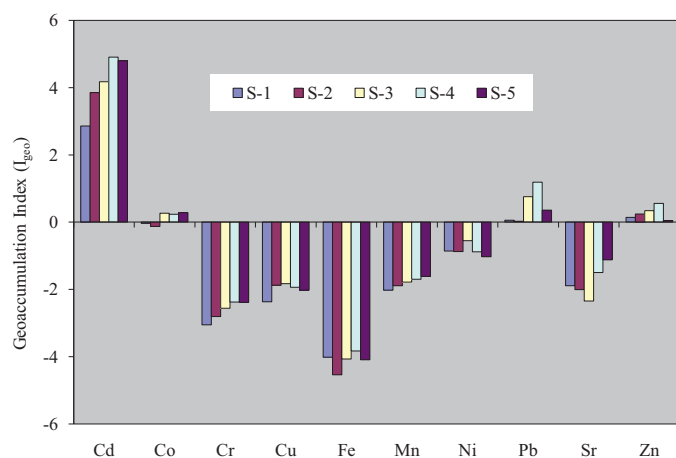**Fig. 5.** Description of enrichment factor (EF) of selected metals at different sites.

Fig. 6. Description of geoaccumulation index (I_{geo}) of selected metals at different sites.

whereas Pb (EF = 17–32) showed severe-very severe enrichment; and Cd (EF = 118–474) demonstrated extremely severe enrichment in the sediments.

3.10. Geoaccumulation index (I_{geo})

I_{geo} is the quantitative measure of the pollution index in the sediments. Any increase in the current levels is envisaged to be anthropogenic in nature. As shown in Fig. 6, the I_{geo} values for the metals revealed that the studied sediments were characterized as heavily to extremely contaminated at the sites S3–S5, heavily contaminated at site S2 and moderately to heavily contaminated at site S1 by Cd. The sediments were uncontaminated to moderately contaminated by Zn (S1–S5), Pb (S1–S3, S5) and Co (S3–S5), and uncontaminated by Cr, Ni, Cu, Fe, Mn, and Sr at all the sites.

4. Conclusions

The mBCR sequential extraction method was applied to investigate the geochemical variations and distribution patterns of selected metals in the sediments from five sites from Mangla Lake, Pakistan. Among the metals, Cr, Cu, Mn, Ni and Zn were found mainly in residual fraction, while Cd, Co and Pb were distributed in exchangeable and reducible fractions. In addition Sr was found predominantly in the exchangeable fraction. The higher percentage of Fe was obtained in both reducible and residual fraction. PCA segregated the metals into four components; Cd–Cr–Ni–Sr; Co–Pb;

Fe–Zn; and Mn–Cu. The ICF showed the high mobility potential of Cd, Sr and Pb to be released from the sediments. According to RAC, the sediments showed medium, high and very high risks for Ni, Cd–Pb–Co and Sr, successively. EF and I_{geo} revealed sever enrichment/accumulation for Co, Pb and Zn, while Cd demonstrated extremely severe enrichment. Overall, Cd, Pb, Sr, Ni and Co emerged as major pollutants in the sediments. CA and GCF identified sites S3, S4 and S5 as pollution hotspots, which were in close proximity to thickly populated urban/semi-urban areas where various anthropogenic activities contributed most of the pollutants in the study area.

Conflicts of interest

The author declare that there is no conflict of interest.

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M. Saleem et al. / Environmental Nanotechnology, Monitoring & Management 4 (2015) 27–36

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