RESEARCH   **Open Access**

Occurrence, risk assessment, and source apportionment of heavy metals in surface sediments from Khanpur Lake, Pakistan

Javed Iqbal and Munir H Shah[*]

Abstract

Background: The present study was carried out to assess the seasonal variations, source apportionment, and risk assessment of heavy metals (Cd, Cr, Cu, Fe, Mn, Pb, and Zn) in the surface sediments from the Khanpur Lake, Pakistan.

Methods: Composite samples are collected and processed to measure the concentrations of heavy metals in $Ca(NO_3)_2$ extract and acid extract of the sediments using flame atomic absorption spectrophotometry.

Results: The highest concentrations in acid extracts of the sediments are found for Fe, followed by Mn, while the least concentrations are noted for Cd. Relatively higher extraction efficiencies in $Ca(NO_3)_2$ extract are observed for Pb and Cd, which also reveal extremely severe enrichment in the sediments as shown by the enrichment factor. Geoaccumulation index shows moderate and strong to extreme pollution of Pb and Cd, respectively, whereas potential ecological risk factor exhibits low to very high risk by Cd; the cumulative ecological risk index reveals low to very high risk of contamination in the sediments as a whole. Principal component analysis and cluster analysis reveal dominant anthropogenic contributions of Cd, Pb, Cr, and Zn.

Conclusion: Measured concentrations of Cd, Cr, Cu, Mn, and Pb in the sediments exceed the sediment quality guideline for the lowest effect levels (LEL), while the concentrations of Cd and Pb are also higher than the effects range low (ERL) values, manifesting occasional adverse biological effects to the surrounding flora and fauna. Moreover, the mean effects range medium (ERM) quotient reveals 21% probability of toxicity in the sediments.

Keywords: Sediment; Metal; Risk assessment; Multivariate analysis; AAS; Pakistan

Background

Contamination of aquatic ecosystems with heavy metals has received much attention due to their toxicity, abundance, and persistence in the environment and subsequent accumulation in aquatic habitats (Arnason and Fletcher 2003). Elevated levels of heavy metals in environmental compartments, such as aquatic sediments, may pose a risk to human health due to their transfer in aquatic media and uptake by living organisms, thereby entering the food chain (Sin et al. 2001; Varol and Sen 2012). Heavy metals may enter a freshwater reservoir from a variety of sources, either natural or anthropogenic (Adaikpoh et al. 2005; Akoto et al. 2008). Generally, in natural ecosystems, most of the metals are present in very low concentrations and are mostly

derived from rock and soil weathering (Reza and Singh 2010; Varol and Sen 2012). Major anthropogenic sources of heavy metal pollution are mining and smelting activities, atmospheric deposition, disposal of untreated/partially treated urban and industrial effluents, metal chelates from different industries, and haphazard use of heavy metal-containing fertilizers and pesticides during agricultural activities (Martin 2000; Nouri et al. 2008; Reza and Singh 2010).

Sediments are ecologically sensitive components of the aquatic ecosystems and are also a reservoir of the contaminants, which take part considerably in maintaining the trophic status for any water reservoir (Singh et al. 2005). Depending upon the physicochemical conditions, sediments can act both as source and sink for nutrients and heavy metals. Hence, sediments are not only considered as carriers of contaminants but also potential secondary sources of contaminants in an aquatic ecosystem.

* Correspondence: munir_qau@yahoo.com
Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

Consequently, the analysis of sediments is a useful method to study the heavy metal pollution in any area (Gielar et al. 2012; Varol and Sen 2012). The toxicity and mobility of the metals in sediments vary among different chemical forms (Cuong and Obbard 2006; Yu et al. 2010). Therefore, the evaluation of distribution and mobility/potential bioavailability of heavy metals in surface sediments is an important step to evaluate the degree of contamination of an aquatic ecosystem (Martin et al. 2009; Sprovieri et al. 2007). Assessment of biologically available fractions of heavy metals helps to evaluate their potential for mobilization and availability to benthic organisms (Rodrigues et al. 2010). Various chemical extraction methods have been suggested to determine the bioavailable fractions of the metals in sediments. Generally, weak acids/electrolytes are used to extract the bioavailable fractions of the metals in sediments (An and Kampbell 2003).

Major objectives of the present study are (i) to measure the concentrations of heavy metals (Cd, Cr, Cu, Fe, Mn, Pb, and Zn) in sediments during summer and winter; (ii) to determine potential ecological risk using enrichment factor (EF), geoaccumulation index (I_{geo}), potential ecological risk factor (E_i), and potential ecological risk index (RI); (iii) to identify risks of potential toxicity by comparison with sediment quality guidelines (SQGs); (iv) to determine potential bioavailability and mobility of the metals; and (v) to define their natural/anthropogenic contributions using multivariate statistical methods. It is anticipated that the study would provide a baseline data regarding the distribution and accumulation of heavy metals in the sediments and would help reduce the contamination by identifying the major pollution sources.

Methods

Study area

Khanpur Lake (longitude 72°56′E and latitude 33°48′N) is situated on the Haro river near the town of Khanpur, about 40 km northwest of Islamabad, Pakistan (Figure 1). It supplies drinking water to the inhabitants of twin cities of Islamabad and Rawalpindi, Pakistan, and irrigation water to
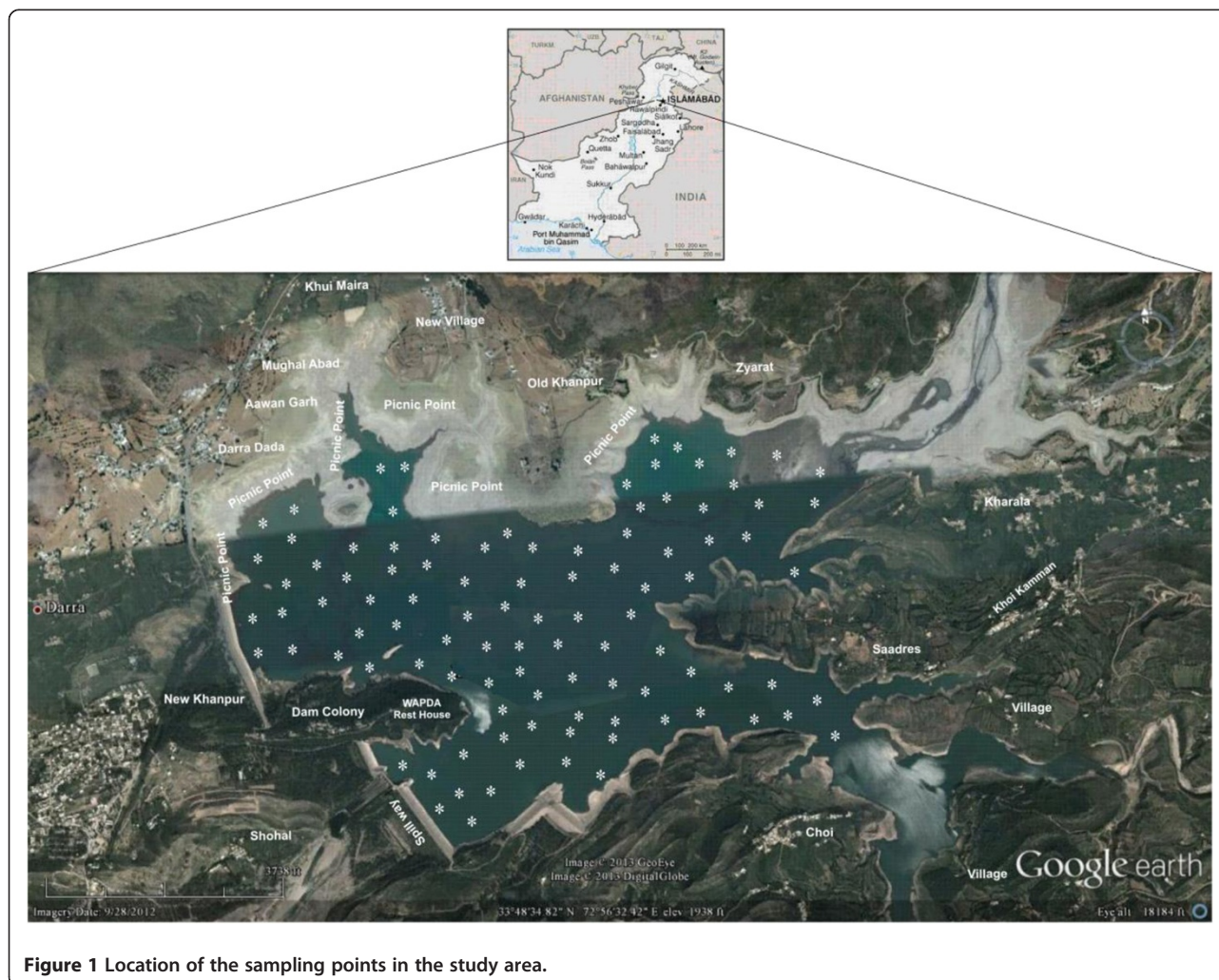

Figure 1 Location of the sampling points in the study area.

the agricultural areas surrounding the cities. It was built in 1983 with the storage capacity of 140 million m^3 of water. It is 51 m high with an average depth of 15 m. The gross storage capacity of the reservoir is 0.132 km^3 with a total catchment area of 798 km^2. The surface area of the reservoir varies from maximum of 1,806 ha to minimum of 215 ha. In past, the lake was leased for commercial exploitation. The area around the lake has been planted with flowering trees and laid out with gardens, picnic spots, and secluded paths. The lake is used for picnics, fishing, boating, sailing, water skating, and diving. Untreated and/or partially treated urban and industrial effluents, road and agricultural run offs, poultry farms wastes, and contaminants released during the recreational use of motorboats are among the suspected sources of pollution in the lake.

Sampling and preservation

A total of 100 composite surface sediment samples from Khanpur Lake, Pakistan, were collected in the summer and winter of 2008. Each sediment sample was a composite of three to five sub-samples from an area of 1 to 2 m^2 and collected using a snapper (Ø 5 cm) in top layer (0 to 10 cm). The sediment samples were taken from the central portion of the snapper with a plastic spatula to avoid any contamination from the metallic parts of the sampler. Before transferring the samples in pre-cleaned Ziploc polythene bags (S. C. Johnson & Son, Inc., Racine, WI, USA), the above water was decanted. The samples were kept in airtight large plastic containers for transport to the laboratory. The sediment samples were then oven-dried, grounded, homogenized, and sealed in pre-cleaned polythene bags and stored in a refrigerator until further processing (Radojevic and Bashkin 1999).

Sample processing and analysis

The samples were processed to assess the $Ca(NO_3)_2$-extractable and acid-extractable fractions of heavy metals. A single-step extraction procedure using 0.1 M $Ca(NO_3)_2$ was applied to the sediment samples at room temperature in order to evaluate the bioavailable metal fractions (An and Kampbell 2003). An aliquot of 5 g of the sample was added to 50-mL solution of 0.1 M $Ca(NO_3)_2$, and the extraction was performed in pre-cleaned glass vessel by shaking on an auto-shaker at 240 vibrations/min for 16 h. A blank sample was also processed with the same amount of reagents without sediment sample. Three replicate extractions were performed for each sample. The final extracts were separated from the solid residues through filtration using a fine (0.45-µm pore) filter paper (An and Kampbell 2003; Radojevic and Bashkin 1999; Rodrigues et al. 2010). To measure the acid-extractable fractions, 1- to 2-g dried sediment sample was digested in a microwave system using an acid mixture of 9 mL HNO_3 and 3 mL HCl (USEPA 2007). Three replicate extractions were performed for each sample. The digests were then filtered through the fine filter paper and made up to 50 mL with double distilled water and stored at 4°C. A blank sample was also processed with the same amount of chemical reagents without sediment sample. Heavy metals (Cd, Cr, Cu, Fe, Mn, Pb, and Zn) in the sediment samples were analyzed using a flame atomic absorption spectrophotometer (Shimadzu AA-670, Kyoto, Japan). The calibration line method was used for quantification of the metals, and the samples were appropriately diluted whenever required (Radojevic and Bashkin 1999; Shah et al. 2012). The optimum analytical conditions used for the quantification of the selected metals on the spectrophotometer are given in Table 1. During sample collection and analysis, strict QA/QC measures were taken including method blanks, analysis of standard reference material, and analysis of duplicate samples. The reagents for the blanks were prepared during each extraction, and all samples were blank-corrected. Standard reference material (NIST SRM-2709) was also used to ensure the reliability of the metal data as shown in Table 1. The measured metal levels closely matched with the certified values. Moreover, reliability of the finished data was also ensured using known spikes and by conducting interlaboratory comparison, and the results were within ±1.5%. Working standards of the metals were prepared from a stock solution of 1,000 mg/L (E-Merck, Darmstadt, Germany) by successive dilutions. The moisture content of each sediment sample was determined by drying separate 5-g sample in an oven (105°C ± 2°C) to constant weight.

Table 1 Description of optimum analytical conditions and analysis of selected metals in SRM

	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Wavelength (nm)	228.8	357.9	324.8	248.3	279.5	217.0	213.9
HC lamp current (mA)	4.0	5.0	3.0	8.0	5.0	7.0	4.0
Slit width (nm)	0.3	0.5	0.5	0.2	0.4	0.3	0.5
Fuel gas flow rate (L/min)	1.8	2.6	1.8	2	1.9	1.8	2
Detection limit (µg/L)	4.0	6.0	4.0	6.0	3.0	10.0	2.0
SRM-certified level (mg/kg)	0.38	130	34.6	35,000	538	18.9	106
SRM-measured level ± SD (mg/kg)	0.36 ± 0.03	138 ± 8	35.2 ± 1.2	34,300 ± 385	547 ± 11	19.3 ± 1.4	109 ± 3.2

The analytical conditions were maintained on AAS using air-acetylene flame, and the standard reference material is SRM-2709.

From this, a correction to dry mass was obtained, which was applied to all reported metal concentrations. All the measurements were made in triplicate.

Statistical analysis

Statistical analysis can be used to evaluate the complex eco-toxicological processes by showing the relationship and interdependency among the variables and their relative weights. Basic statistical parameters, such as minimum, maximum, mean, median, standard error (SE), and skewness, were computed along with correlation study. Multivariate techniques have been used for evaluation and characterization of analytical data (Fadigas et al. 2010). Principal component analysis (PCA) and cluster analysis (CA) are among the most popular methods. The PCA finds out the diagonalization of the covariance or correlation matrix transforming the original chemical measurements into linear combinations of these measurements, which are the principal components (PCs). It rotates the coordinate space axes so that the explained variance of each PC is maximized. This technique allows for data reduction from higher to lower dimensional spaces to simplify their representation. Nonetheless, CA demonstrates the similarities between variables by examining the interpoint distances representing all possible variables in the higher dimensional space. The PCA was performed using varimax normalized rotation on the dataset, and the CA was applied to the standardized matrix of the samples using Ward's method, and the results are reported in the form of dendrograms. PCA and CA complement each other and have been widely used in environmental studies (Gielar et al. 2012; Iqbal and Shah 2011; Shah et al. 2012; Singh et al. 2005).

Pollutant indicators and risk assessment

To gauge the degree of contamination and to distinguish natural and anthropogenic inputs, EFs, I_{geo}, E_i, and RI are computed (Cukrov et al. 2011; Hakanson 1980; Muller 1969). EFs are calculated (Cukrov et al. 2011; Iqbal and Shah 2011; Luoma and Rainbow 2008; Tessier et al. 2011) by comparing the measured metal levels to the pre-industrial levels (Lide 2005). In order to avoid the overestimation or underestimation of the enrichment; geochemical normalization based on the concentration of a conservative element is commonly employed. The purpose of normalization is to correct changes in the nature of sediments, which may influence the contaminant distribution. Various conservative elements may be used: Al, Fe, Th, Ti, Zr, etc. (Larrose et al. 2010; Reimann and de Caritat 2005). Iron is chosen as the conservative element for normalization in this work. The interest of using Fe content is its relationship to the abundance of clay and other aluminum silicates in the sediments. Its contents are influenced by natural sedimentation and the effects of enhanced erosion, but not by pollution (Iqbal and Shah 2011). The normalized

EF is usually computed as double ratios of the target element and Fe as a reference element in the examined sediments and Earth's crust using the following relationship:

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

where $[X/Fe]_{sample}$ and $[X/Fe]_{crust}$ refer, respectively, to the ratios of mean concentrations (mg/kg, dry weight) of the target element and Fe in the sediments and continental crust (Lide 2005).

The I_{geo} enables the assessment of contamination by comparing the measured and pre-industrial concentrations of the metals in the Earth's crust (Loska et al. 2004; Muller 1969). It is computed using the following relationship:

$$I_{geo} = \log_2 \left(C_n \middle/ 1.5B_n \right),$$

where C_n is the measured concentration of the element in the sediment samples, and B_n is the geochemical background value in the Earth's crust (Lide 2005). Factor 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithogenic variations.

RI is introduced to assess the degree of heavy metal pollution in sediments, which was originally introduced by Hakanson (1980), according to the toxicity of heavy metals and the response of the environment:

$$RI = \sum E_i$$
$$E_i = T_i f_i$$
$$f_i = C_i / C_b,$$

where RI is computed as the sum of all risk factors in sediments, E_i is the monomial potential ecological risk factor for individual factors, and T_i is the metal toxic factor. Based on the standardized heavy metal toxic factor developed by Hakanson (1980), the order of the level of heavy metal toxicity is Cd > Pb = Cu > Cr > Zn. The toxic factors for the metals are 30, 5, 5, 2, and 1, respectively. f_i is the metal pollution factor, C_i is the concentration of metal in the sediments, and C_b is the reference value of a given metal in the Earth's crust (Lide 2005).

Multiple contamination which is often encountered in natural environments affected by human activities is also calculated in terms of mean-effects range medium-quotient (m-ERM-Q) by the following relationship (de Vallejuelo et al. 2010; Long and MacDonald 1998; Tessier et al. 2011):

$$m-ERM-Q = \frac{\sum_{i=1}^{n} C_i / ERM_i}{n},$$

where C_i is the concentration of a metal in a sediment, ERM_i is the ERM value for metal i, and n is the number of metals.

Results and discussion

Distribution of heavy metals in the sediments

Concentrations of heavy metals in acid extracts of the sediments during summer and winter in terms of statistical distribution parameters are shown in Table 2. During summer, the data reveal dominant mean level of Fe (4,630 mg/kg), followed by Mn (447.5 mg/kg), while the average concentration of Cd (1.883 mg/kg) is the lowest. On the average basis, the metals follow a decreasing concentration order: Fe > Mn > Zn > Cu > Cr > Pb > Cd. Among the metals, Fe indicates almost comparable mean and median levels with lower skewness, indicating relatively symmetrical distribution in acid extract of the sediments. The counterpart statistical data during winter show the highest average levels of Fe (3,791 mg/kg), followed by Mn (321.4 mg/kg), whereas Pb (18.24 mg/kg) and Cd (2.457 mg/kg) are found at relatively lower levels. On the mean basis, the metals exhibit a decreasing concentration order: Fe > Mn > Zn > Cr > Cu > Pb > Cd. Relatively normal distribution is revealed by Cd and Pb, which are also associated with lower skewness. Maximum dispersion in terms of SE is exhibited by Fe. Overall, significantly elevated average levels of the metals (except Cd and Cr) are noticed during summer compared with winter (Table 2). It could be due to the leaching of the metals into the reservoir from the roadside and agricultural runoffs during wet summer season.

Correlation study

The correlation coefficient matrix of heavy metals in the acid extract of the sediments during summer and winter is given in Table 3. During summer, strong correlations of Fe with Mn and Cu, Cr with Zn, and Cu with Mn are noted. Some other significant relationships of Pb with Cd and Cr are also observed. However, Pb and Zn show negative associations with Cu, Fe, and Mn, revealing their opposing distribution in the sediments during summer. The counterpart data related to the metal levels in the sediments during winter indicate strong correlations of Zn with Cu and Mn, Cu with Mn, and Cr with Cd and Cu, thus manifesting close association of these metals which might share common sources. Some significant correlations for Pb with Cr, Cu, Mn, and Zn are also observed. Fe does not show any significant relationship with other heavy metals in the sediments during winter, suggesting its independent variations in the sediments.

Pollution indices

The range and mean EF values of heavy metals in acid extract of the sediments during summer and winter are shown in Figure 2a. Seven degrees of contamination are commonly defined (Birch et al. 2003): EF < 1 indicates no enrichment, EF < 3 minor enrichment, EF = 3 to 5 moderate enrichment, EF = 5 to 10 moderately severe enrichment, EF = 10 to 25 severe enrichment, EF = 25 to 50 very severe enrichment, and EF > 50 extremely severe enrichment. During summer, on the average basis, Cr reveals moderate enrichment, Cu and Mn indicate moderately severe enrichment, Zn manifests severe enrichment, Pb shows very severe enrichment, and Cd illustrates extremely severe enrichment in the sediments. The geochemical normalization study during winter reveals that Cr, Cu, and Mn indicate moderately severe

Table 2 Statistical summary of heavy metal distribution in acid extract and Ca(NO₃)₂ extract of the sediments

		Summer ($n = 50$)					Winter ($n = 50$)					p value
		Min	Max	Mean	SE	Skew	Min	Max	Mean	SE	Skew	
Acid extract	Cd	0.196	4.500	1.883	0.234	0.584	0.149	5.183	2.457	0.235	−0.084	<0.05
	Cr	11.35	63.45	34.66	2.293	−0.262	23.82	68.97	37.65	1.543	1.790	Non-significant
	Cu	25.15	49.39	36.84	1.285	−0.072	18.22	51.53	28.05	1.314	1.166	<0.05
	Fe	3,835	5,186	4,630	57.83	−0.350	3,523	4,182	3,791	30.95	0.426	<0.05
	Mn	236.2	836.7	447.5	32.97	0.713	167.7	886.0	321.4	26.00	2.234	<0.05
	Pb	9.739	78.48	33.71	3.419	0.771	0.412	39.03	18.24	1.966	−0.003	<0.01
	Zn	70.71	114.4	86.09	2.032	0.650	42.24	115.2	61.90	2.459	2.190	<0.05
Ca(NO₃)₂ extract	Cd	0.004	0.122	0.058	0.006	−0.081	0.016	0.146	0.071	0.006	0.175	Non-significant
	Cr	0.042	0.546	0.217	0.027	0.794	0.008	0.478	0.230	0.023	0.061	Non-significant
	Cu	0.008	0.220	0.098	0.008	0.212	0.012	0.134	0.073	0.006	−0.201	<0.05
	Fe	0.020	28.50	2.069	0.985	4.415	0.248	1.218	0.658	0.053	0.314	<0.01
	Mn	0.004	0.274	0.078	0.012	1.149	0.010	0.072	0.042	0.003	0.178	<0.01
	Pb	0.206	2.032	1.192	0.085	−0.343	0.140	2.082	1.205	0.087	−0.254	Non-significant
	Zn	0.010	0.656	0.179	0.023	1.972	0.056	0.186	0.118	0.007	0.175	<0.05

The heavy metal distribution is expressed in milligrams per kilogram.

Table 3 Correlation coefficients (r)* matrix for heavy metals in acid extract of sediments during summer and winter

	Cd	Cr	Cu	Fe	Mn	Pb	Zn
Cd	1	0.580	0.389	−0.029	0.473	0.181	0.223
Cr	0.320	1	0.657	0.087	0.319	0.412	0.345
Cu	0.171	0.153	1	0.143	0.685	0.480	0.803
Fe	0.071	−0.056	0.615	1	0.126	0.151	−0.016
Mn	0.086	−0.031	0.863	0.551	1	0.425	0.619
Pb	0.362	0.432	−0.068	−0.187	−0.087	1	0.427
Zn	0.103	0.540	−0.028	−0.208	−0.245	0.062	1

Values for summer are below the diagonal, and those for winter are above the diagonal. *r values >0.330 or <−0.330 are significant at $p < 0.01$.

enrichment; Pb and Zn explicate severe enrichment, and Cd illuminates extremely severe enrichment. Overall, Cd emerge as the major pollutant during both seasons; Pb poses severe to extremely severe enrichment during summer and minor to very severe enrichment during winter. Zn causes severe enrichment during both seasons. Mostly, elevated degree of pollution by the metals is noted during summer than during winter.

The lowest, mean, and highest values of I_{geo} in acid extract of the sediments during summer and winter are illustrated in Figure 2b. The following categorizations are given by Muller (1969) for geoaccumulation index: I_{geo} < 0 indicates unpolluted, I_{geo} = 0 to 1 unpolluted to moderately polluted, I_{geo} = 1 to 2 moderately polluted, I_{geo} = 2 to 3 moderately to strongly polluted, I_{geo} = 3 to 4 strongly polluted, I_{geo} = 4 to 5 strongly to extremely polluted, and I_{geo} > 5 demonstrates extremely polluted. The highest category reflects at least a 100-time enrichment above the background values. As shown in the figure, during summer, Cd and Pb pose strong to extreme contamination and moderate contamination, respectively. However, the remaining metals exhibit practically uncontamination in the sediments. During winter, Cd indicates strong to extreme pollution; Zn causes unpolluted to moderate pollution, whereas Pb shows least to moderate contamination.

Ecological risk assessment

The range and mean E_i values of the heavy metals in acid extract of the sediments during summer and winter are shown in Figure 2c. The following categorization is given by Hakanson (1980) for E_i: E_i < 40 demonstrates low risk, E_i = 40 to 80 moderate risk, E_i = 80 to 160 considerable risk, E_i = 160 to 320 great risk, and E_i > 320 demonstrates very great risk. The categorization related to RI is also suggested by Hakanson (1980): RI < 65 explicates low risk, RI = 65 to 130 moderate risk; RI = 130 to 260 considerable risk, and RI > 260 explicates very high risk. The results elucidate that Cd causes low to very high risk, while the rest of the metals explicate low

risk in the sediments during both seasons. Overall, the cumulative potential risk index (RI = 45.91 to 935 during summer and RI = 31.87 to 1,058 during winter) reveals low to very high risk of the sediments during both seasons. However, relatively higher potential ecological risk is observed during winter compared to summer.

Source apportionment

One of the important aspect of the present study is the source apportionment of the metals in sediments using PCA and CA. The principal component loadings of the heavy metals in acid extract of the sediments during summer and winter are given in Table 4, whereas the corresponding CA is shown in Figure 3. During summer, two PCs are extracted with eigenvalues more than 1, explaining about 60% of the total variance. The first PC (36.14% variance) reveals elevated loadings of Fe, Mn, and Cu, supported by their mutual cluster in CA. These metals are likely to be contributed by lithogenic processes such as soil erosion and rock weathering. The second PC (23.77% variance) shows significant loadings of Pb, Cd, Cr, and Zn supported by their shared cluster and are mainly contributed by automobile emissions, agricultural runoff, and untreated urban wastes. The counterpart data during winter also yield two PCs with eigenvalues greater than 1, explaining more than 66% of the total variance. PC1 (51.09% variance) exhibits higher loadings for Zn, Cu, Cr, Mn, Pb, and Cd, which are predominantly contributed by transportation activities, untreated urban wastes, and agricultural runoff. The cluster analysis also shows a joint cluster for these metals. PC2 (15.22% variance) reveals the natural/lithogenic contribution as manifested by the elevated loadings of Fe only which shows almost independent pattern in CA.

Sediment quality guidelines

The assessment of acid-extractable metal levels in the sediments is the first step to gauge the pollution of the water reservoir. However, it does not provide information on the potential toxicity to the benthic flora and fauna in the reservoir. For this purpose, numerous sediment quality guidelines are used to protect aquatic biota from the harmful and toxic effects related with sediment-bound contaminants (Caeiro et al. 2005; McCready et al. 2006; Spencer and Macleod 2002). These guidelines evaluate the degree to which the sediment-associated chemical status might adversely affect the aquatic organisms and therefore are designed for the interpretation of sediment quality. SQGs have been developed for both freshwater and marine ecosystems to represent threshold chemical concentrations associated with the presence or absence of biological effects on communities (Caeiro et al. 2005; Long and
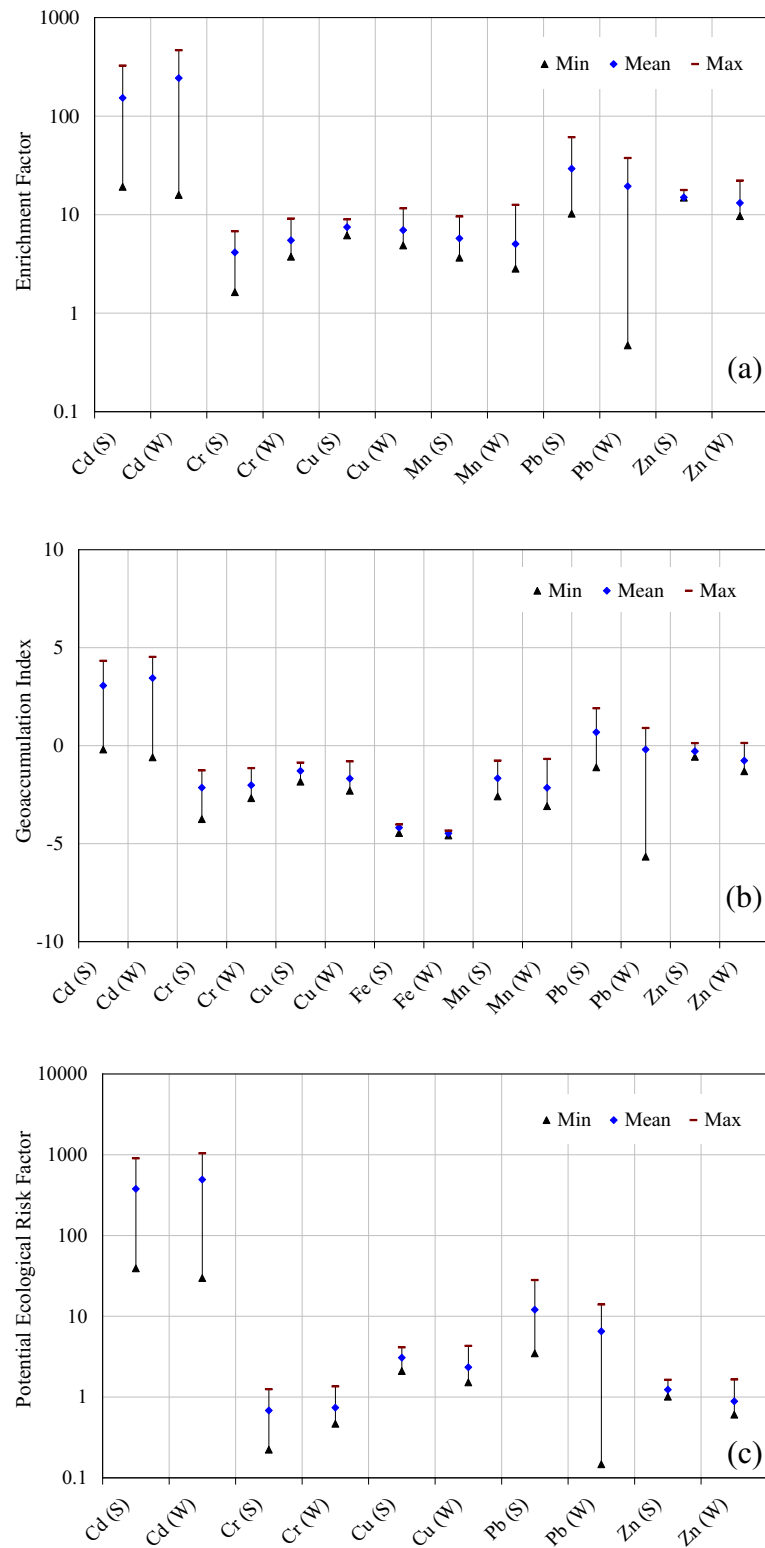
Figure 2 Description of the different parameters. Description of **(a)** enrichment factor (EF), **(b)** geoaccumulation index (I_{geo}) and **(c)** potential ecological risk factor (E_i) of heavy metals in acid extract of sediments during summer (S) and winter (W).

Table 4 Principal component loadings of heavy metals in acid extract of sediments during summer and winter

	Summer		Winter	
	PC1	PC2	PC1	PC2
Eigenvalue	2.530	1.664	3.576	1.065
Percentage of total variance	36.14	23.77	51.09	15.22
Percentage of cumulative variance	36.14	59.91	51.09	66.30
Cd	0.131	0.733	0.506	−0.139
Cr	0.284	0.666	0.838	−0.015
Cu	0.914	0.144	0.884	0.179
Fe	0.800	−0.108	−0.035	0.951
Mn	0.913	0.020	0.835	0.140
Pb	−0.179	0.714	0.557	0.388
Zn	−0.273	0.393	0.876	0.011

MacDonald 1998; MacDonald et al. 2000; Thompson et al. 2005; Wenning et al. 2005). These guidelines have been widely used to screen sediment contamination by comparing the concentrations in sediments with the corresponding quality guidelines in aquatic ecosystems (Caeiro et al. 2005; MacDonald et al. 2000). It is important to determine whether the estimated concentrations of heavy metals in sediments pose a threat to aquatic life, and they are assessed by two sets of sediment quality guidelines: (i) lowest effect level (LEL) and severe effect level (SEL) and (ii) effects range low (ERL) and effects range medium (ERM) (MacDonald et al. 2000). These two sets of numerical SQGs are directly applied to assess the possible risk associated with heavy metal contamination in the sediments. It is interpreted that LEL and ERL as the concentrations below which adverse biological effects rarely occur. Hence, these are considered to
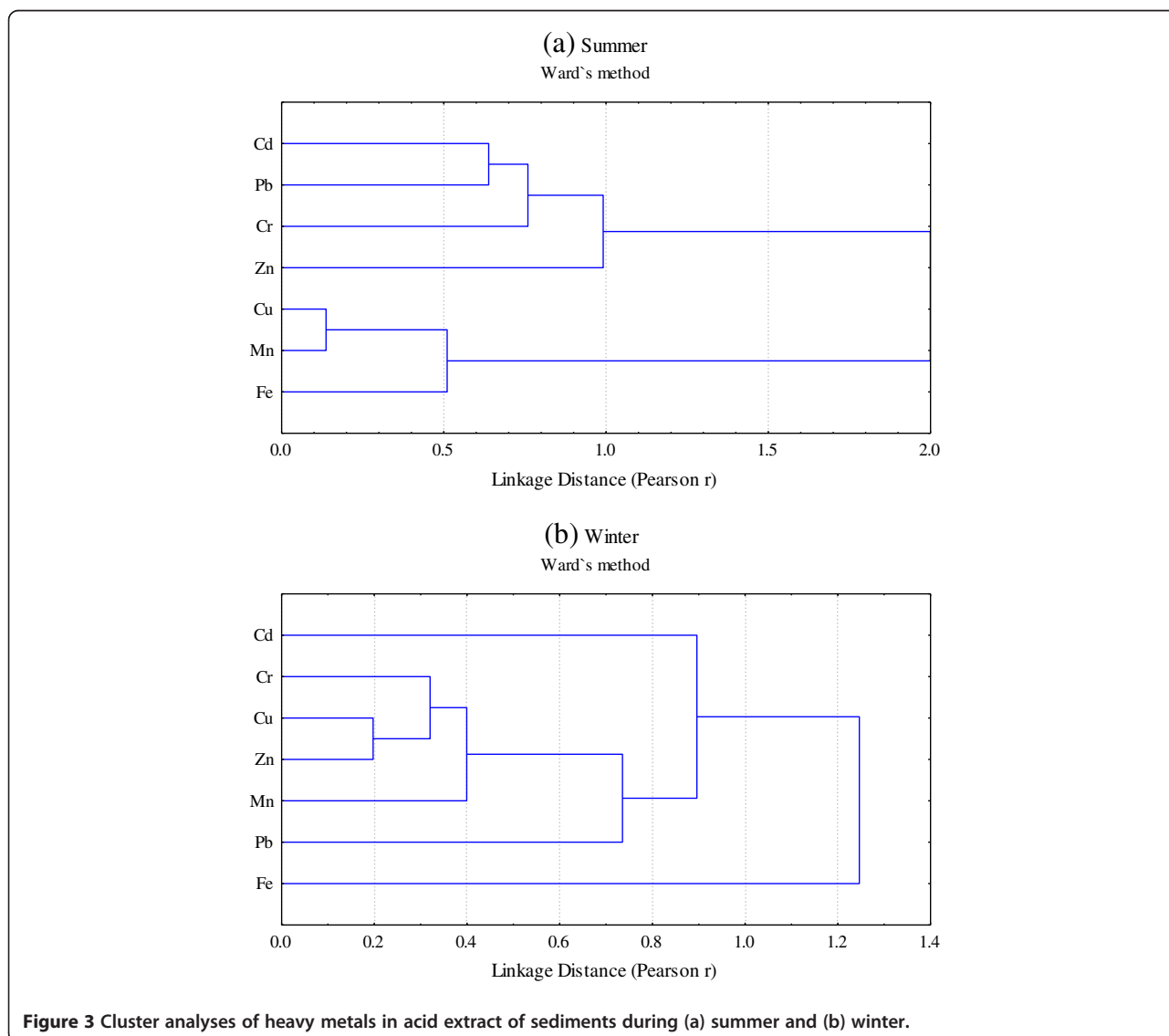

Figure 3 Cluster analyses of heavy metals in acid extract of sediments during (a) summer and (b) winter.

provide a high level of protection for aquatic organisms. Similarly, SEL and ERM refer to the concentrations above which adverse biological effects frequently occur. Hence, these are considered to provide a lower level of protection for aquatic organisms (Long and MacDonald 1998; MacDonald et al. 2000).

The description of SQGs and sediment classification along with the results related to the sediments from Khanpur Lake during summer and winter is presented in Table 5, while the percent contribution of heavy metals towards potential acute toxicity in the sediments during summer and winter is depicted in Figure 4. During summer, the measured levels of Cd, Cr, Cu, Mn, and Pb are found to be higher than the LEL values in 87%, 100%, 100%, 37%, and 37% sediment samples, respectively. It depicts that these metals could pose moderate impact on the biota (Graney and Eriksen 2004). On the other hand, the concentrations of Fe and Zn are found to be lower than the LEL levels in 100% sediment samples, demonstrating that these metals cause little or no

impact on biota in the lake. Similarly, the measured levels of Cd, Cr, Cu, and Zn are found to be lower than the ERL values in 100% sediment samples, revealing that these metals are not associated with adverse health effects to the dwelling biota (MacDonald et al. 2000). However, Pb levels are found to be higher in 37% sediment samples, manifesting that Pb is associated with frequent adverse biological effects to the underlying organisms (MacDonald et al. 2000). Furthermore, potential acute toxicity (ΣTUs) study shows that the mean levels of toxic units (TUs) for heavy metals follow a decreasing order: Cd > Cr > Pb > Zn > Cu. It indicates relatively higher contributions of Cd, Cr, and Pb to ΣTUs (i.e., 31%, 22%, and 21%, respectively; Figure 4) (Pedersen et al. 1998). Nevertheless, Cu (11%) is the minor contributor to ΣTUs compared with the other heavy metals. The levels of ΣTUs range from 0.64 to 3.45 with a mean value of 1.75 in the sediments. Based on the USEPA sediments classification (Giesy and Hoke 1990), Cr, Cu, and Zn show moderate contamination, Mn and Pb exhibit heavy pollution, and Cd

Table 5 Description of sediment classification and sediment quality guidelines in acid extract of sediments in two seasons

		Cd	Cr	Cu	Fe	Mn	Pb	Zn
Sediment classification	Non-polluted	-	<25	<25	<17,000	<300	<40	<90
	Moderately polluted	-	25 to 75	25 to 50	17,000 to 25,000	300 to 500	40 to 60	90 to 200
	Heavily polluted	>6	>75	>50	>25,000	>500	>60	>200
Sediment quality guidelines (SQGs)	LEL	0.6	26	16	20,000	460	31	120
	SEL	10	110	110	40,000	1,100	250	820
	ERL	5	80	70	-	-	35	120
	ERM	9	145	390	-	-	110	270
Percentage of samples (summer)	Non-polluted	100	-	-	100	23	63	67
	Moderately polluted	-	100	100	-	43	23	33
	Heavily polluted	-	-	-	-	34	14	-
	<LEL	13	-	-	100	63	63	100
	≥LEL and <SEL	87	100	100	-	37	37	-
	>SEL	-	-	-	-	-	-	-
	<ERL	100	100	100	-	-	63	100
	≥ERL and <ERM	-	-	-	-	-	37	-
	>ERM	-	-	-	-	-	-	-
Percentage of samples (winter)	Non-polluted	100	3.0	40	100	53	100	97
	Moderately polluted	-	97	57	-	44	-	3.0
	Heavily polluted	-	-	3.0	-	3.0	-	
	<LEL	10	3.0	-	100	90	93	100
	≥LEL and <SEL	90	97	100	-	10	7.0	-
	>SEL	-	-		-	-	-	-
	<ERL	97	100	100	-	-	93	100
	≥ERL and <ERM	3.0	-	-	-	-	7.0	-
	>ERM	-	-	-	-	-	-	-

The units of metals are expressed in milligrams per kilogram. LEL, lowest effect level; SEL, severe effect level; ERL, effect range low; ERM, effect range median.
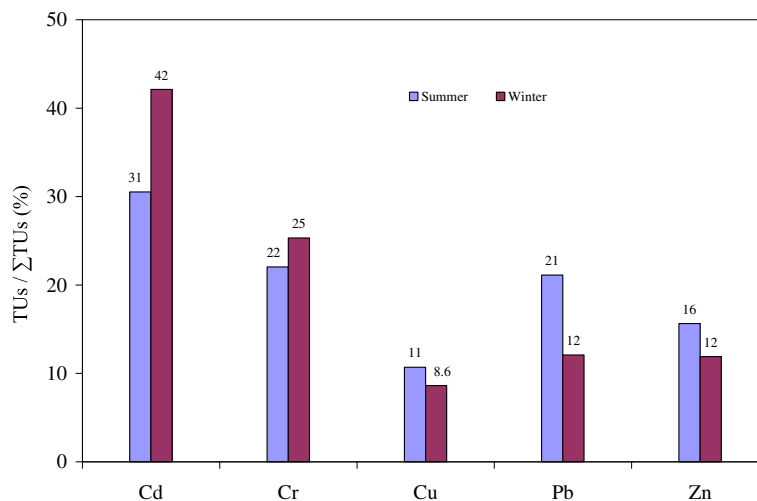
Figure 4 Percent contribution of heavy metals to ΣTUs in acid extract of sediments during summer and winter.

and Fe reveal little or no contamination in the sediments during summer. It demonstrates that Cr, Cu, Zn, Pb, and Mn are the major contributors toward the gross pollution of the water reservoir.

During winter, the measured levels of Cd, Cr, Cu, Mn, and Pb in the sediments are found to be higher than the LEL values in 90%, 97%, 100%, 10%, and 7.0% samples, respectively. It reveals moderate impact on the biota health. The observed values of Fe and Zn are found to be lower than the LEL values in 100% sediment samples, indicating that these metals are not associated with adverse impact on the biota (Graney and Eriksen 2004). The ERL and ERM SQGs manifest that Cd and Pb levels exceed the ERL values in 3.0% and 7.0% sediment

samples, respectively, demonstrating that these metals are associated with occasional adverse health hazards to the surrounding biota (MacDonald et al. 2000). The concentrations of Cr, Cu, and Zn are lower than the ERL values in 100% sediment samples, demonstrating little or no undesirable health hazards. The potential acute toxicity study reveals that the average levels of TUs for heavy metals follow a decreasing order: Cd > Cr > Pb > Zn > Cu. It illustrates that Cd, Cr, and Pb are the major contributors to ΣTUs (i.e., 42%, 25%, and 12%, respectively; Figure 4), while Cu (8.6%) is a minor contributor (Pedersen et al. 1998). The values of ΣTUs range from 0.54 to 3.29 with an average value of 3.29 in the sediments. Based on the USEPA sediments classification
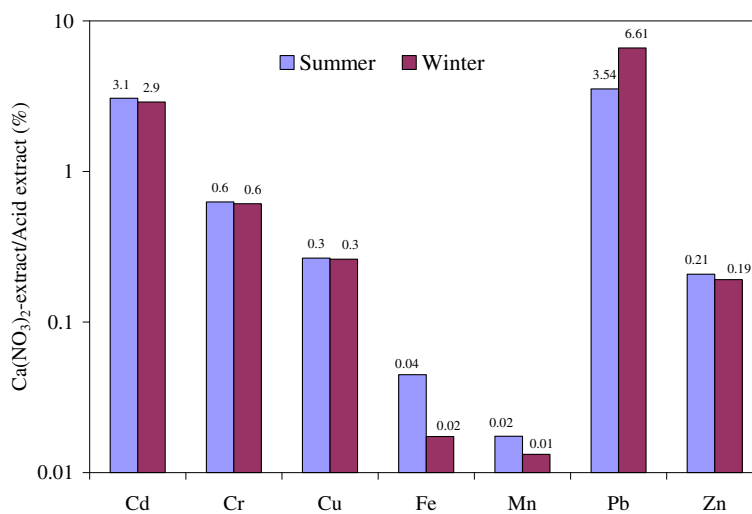

Figure 5 Percent extraction of heavy metals in Ca(NO$_3$)$_2$ extract of sediments during summer and winter.

(Giesy and Hoke 1990), Cd, Fe, and Pb may pose little or no pollution. Cr and Zn cause moderate contamination, and Cu and Mn exhibit heavy pollution in the sediments. Consequently, Cr, Cu, Mn, and Zn emerge as the major pollutants in the water reservoir during winter. Overall, the SQG results lead to the conclusion that the metals, such as Cd, Cr, Cu, Mn, and Pb are of concern during both seasons. Potential acute toxicity results demonstrate that Cd, Cr, and Pb are the major toxicants, while Zn and Cu are the minor pollutants during both seasons. However, relatively higher potential acute toxicity is observed during summer than during winter.

From the ecotoxicological dataset obtained for the US Coasts, Long et al. (1998) have defined several classes of toxicity probability for benthic biota: m-ERM-Q < 0.1 has a 9% probability of being toxic (based on amphipod survival test), m-ERM-Q between 0.11 and 0.5 has 21% probability of toxicity, m-ERM-Q between 0.51 and 1.5 has a probability of 49% to be toxic, and m-ERM-Q > 1.50 has 76% probability of toxicity. In the present study, the m-ERM-Q values range from 0.159 to 0.408 and 0.126 to 0.337 with the average values of 0.247 and 0.200 during summer and winter, respectively. Consequently, the metals pose approximately 21% probability of toxicity to the benthic organisms in the lake during both seasons.

Bioavailability of heavy metals in the sediments

Potential toxicity of heavy metals in the sediments is also assessed by the measurement of mobile metal concentrations. The statistical distribution parameters related to the concentrations of heavy metals in $Ca(NO_3)_2$ extract of the sediments during summer and winter are given in Table 2, whereas their percent extraction in $Ca(NO_3)_2$ extract is shown in Figure 5. The summer results reveal Fe as having the highest contributions (2.069 mg/kg), while the measured levels of Mn and Cd are the least. Nonetheless, the winter results demonstrate an elevated concentration of Pb (1.205 mg/kg), and the mean level of Mn is the lowest. On the percent extraction basis, the metals follow identical decreasing sequence during summer and winter: Pb > Cd > Cr > Cu > Zn > Fe > Mn. Moreover, there are no direct relationships among the $Ca(NO_3)_2$-extractable and acid-extractable fractions of the metals in sediments. The $Ca(NO_3)_2$-extractable recoveries are found to be within approximately 11% during summer and 15% during winter of the acid-extractable metal concentrations (Figure 5). Since element bioavailability is related to its solubility, extractable metal concentrations may correspond to the bioavailable concentrations (An and Kampbell 2003). The results demonstrate that Pb and Cd show the maximum extraction efficiencies, mobilities, and bioavailabilities, followed by Cr, while Fe and Mn manifest the least during both seasons.

Accordingly, Pb, Cd, and Cr exhibit higher mobility and higher potential toxicity to the surrounding biota, while Fe and Mn show least mobility and bioavailability to the benthic biota in the water reservoir.

Conclusions

The present study is primarily related to the evaluation of the distribution, correlation, source apportionment, contamination, and risk assessment of the heavy metals in surface sediments from Khanpur Lake, Pakistan. The study shows significantly divergent metal levels for most of the cases in the sediments during summer and winter. Most of the metals exhibit random distribution and diverse correlations in the sediments. Extremely severe enrichment is noted for Cd and Pb, while Zn shows severe enrichment. Moderate pollution is associated with Pb levels; strong to extreme pollution is shown by Cd, which is also associated with very high risk. On the whole, RI shows low to very high risk of contamination in the sediments. Multivariate PCA and CA manifest dominantly anthropogenic contributions of Pb, Cd, Cr, and Zn in the sediments. Comparison of heavy metal contents in the sediments with quality guidelines indicates adverse biological effects to the surrounding flora and fauna due to elevated levels of the metals. The m-ERM-Q study reveals 21% probability of toxicity due to the metals in the sediments. The potential toxicity, mobility, and bioavailability manifest that Cd and Pb are more mobile and available to the benthic flora and fauna. The present investigation clearly indicates that the sediments from freshwater reservoir are contaminated with some toxic heavy metals. Consequently, there is a dire need to reduce/regulate the anthropogenic sources of pollution in the study area.

References
Adaikpoh EO, Nwajei GE, Ogala JE (2005) Heavy metals concentrations in coal and sediments from River Ekulu in Enugu, coal city of Nigeria. J Appl Sci Environ Manage 9:5–8
Akoto O, Bruce TN, Darko G (2008) Heavy metals pollution profiles in streams serving the Owabi reservoir. Afr J Environ Sci Technol 2:354–359

An YJ, Kampbell DH (2003) Total, dissolved, and bioavailable metals at Lake Texoma marinas. Environ Pollut 122:253–259

Arnason JG, Fletcher BA (2003) A 40+ year record of Cd, Hg, Pb, and U deposition in sediments of Patroon Reservoir, Albany County, NY, USA. Environ Pollut 123:383–391

Birch G et al (2003) A scheme for assessing human impacts on coastal aquatic environments using sediments. In: Coastal GIS. Wollongong University Papers in Center for Maritime Policy, Australia, p 14

Caeiro S, Costa MH, Ramos TB, Fernandez F, Silveira N, Coimbra A, Medeiros G, Painho M (2005) Assessing heavy metal contamination in Sado estuary sediment: an index analysis approach. Ecol Indicat 5:151–169

Cukrov N, Bilinski SF, Hlaca B, Barisic D (2011) A recent history of metal accumulation in the sediments of Rijeka harbor, Adriatic Sea, Croatia. Mar Pollut Bull 62:154–167

Cuong DT, Obbard JP (2006) Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. Appl Geochem 21:1335–1346

de Vallejuelo SFO, Arana G, de Diego A, Madariaga JM (2010) Risk assessment of trace elements in sediments: the case of the estuary of the Nerbioi–Ibaizabal River (Basque Country). J Hazard Mater 181:565–573

Fadigas JC, dos Santos AMP, de Jesus RM, Lima DC, Fragoso WD, David JM, Ferreira SLC (2010) Use of multivariate analysis techniques for the characterization of analytical results for the determination of the mineral composition of kale. Microchem J 96:352–356

Gielar A, Rybicka EH, Moller S, Einax JW (2012) Multivariate analysis of sediment data from the upper and middle Odra River (Poland). Appl Geochem 27:1540–1545

Giesy JP, Hoke RA (1990) Freshwater sediment quality criteria: toxicity bioassessment. In: Baudo R, Giesy JP, Muntao M (eds) Sediment: chemistry and toxicity of in-place pollutants. Lewis Publishers, Ann Arbor, MI, p 39

Graney JR, Eriksen TM (2004) Metals in pond sediments as archives of anthropogenic activities: a study in response to health concerns. Appl Geochem 19:1177–1188

Hakanson L (1980) An ecological risk index for aquatic pollution control: a sedimentological approach. Water Res 14:975–1001

Iqbal J, Shah MH (2011) Distribution, correlation and risk assessment of selected metals in urban soils from Islamabad, Pakistan. J Hazard Mater 192:887–898

Larrose A, Coynel A, Schafer J, Blanc G, Masse L, Maneux E (2010) Assessing the current state of the Gironde Estuary by mapping priority contaminant distribution and risk potential in surface sediment. Appl Geochem 25:1912–1923

Lide DR (2005) CRC handbook of Chemistry and Physics, Geophysics, Astronomy, and Acoustics. Section 14, Abundance of elements in the Earth's crust and in the sea, 85th edn. CRC Press, Boca Raton, FL

Long ER, MacDonald DD (1998) Recommended uses of empirically derived, sediment quality guidelines for marine and estuarine ecosystems. Hum Ecol Risk Assess 4:1019–1039

Long ER, Field LJ, McDonald DD (1998) Predicting toxicity in marine sediments with numerical sediment quality guidelines. Environ Toxicol Chem 17:714–727

Loska K, Wiechula D, Korus I (2004) Metal contamination of farming soils affected by industry. Environ Int 30:159–165

Luoma SN, Rainbow PS (2008) Metal contamination in aquatic environments: science and lateral management. Cambridge University Press, Cambridge, UK, pp 91–103

MacDonald DD, Ingersoll CG, Berger TA (2000) Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch Environ Contam Toxicol 39:20–31

Martin CW (2000) Heavy metal trends in floodplain sediments and valley fill, River Lahn, Germany. Catena 39:53–68

Martin J, Cabeza JAS, Eriksson M, Levy I, Miquel JC (2009) Recent accumulation of trace metals in sediments at the DYFAMED site (Northwestern Mediterranean Sea). Mar Pollut Bull 59:146–153

McCready S, Birch GF, Long ER (2006) Metallic and organic contaminants in sediments of Sydney Harbour, Australia and vicinity—a chemical dataset for evaluating sediment quality guidelines. Environ Int 32:455–465

Muller G (1969) Index of geoaccumulation in sediments of the Rhine River. J Geol 2:108–118

Nouri J, Mahvi AH, Jahed GR, Babaei AA (2008) Regional distribution pattern of groundwater heavy metals resulting from agricultural activities. Environ Geol 55:1337–1343

Pedersen F, Sjobrnestad E, Andersen HV, Kjolholt J, Poll C (1998) Characterization of sediments from Copenhagen harbour by use of biotests. Water Sci Technol 37:233–240

Radojevic M, Bashkin VN (1999) Practical environmental analysis. The Royal Society of Chemistry, Cambridge, UK

Reimann C, de Caritat P (2005) Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. Sci Total Environ 337:91–107

Reza R, Singh G (2010) Heavy metal contamination and its indexing approach for river water. Int J Environ Sci Technol 7:785–792

Rodrigues SM, Henriques B, Coimbra J, da Silva EF, Pereira ME, Duarte AC (2010) Water-soluble fraction of mercury, arsenic and other potentially toxic elements in highly contaminated sediments and soils. Chemosphere 78:1301–1312

Shah MH, Iqbal J, Shaheen N, Khan N, Choudhary MA, Akhter G (2012) Assessment of background levels of trace metals in water and soil from a remote region of Himalaya. Environ Monit Assess 184:1243–1252

Sin SN, Chua H, Lo W, Ng LM (2001) Assessment of heavy metal cations in sediments of Shing Mun River, Hong Kong. Environ Int 26:297–301

Singh KP, Malik A, Sinha S, Singh VK, Murthy RC (2005) Estimation of source of heavy metal contamination in sediments of Gomti River (India) using principal component analysis. Water Air Soil Pollut 166:321–341

Spencer KL, Macleod CL (2002) Distribution and partitioning of heavy metals in estuarine sediment cores and implications for the use of sediment quality standards. Hydrol Earth Syst Sci 6:989–998

Sprovieri M, Feo ML, Prevedello L, Manta DS, Sammartino S, Tamburrino S, Marsella E (2007) Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbor (southern Italy). Chemosphere 67:998–1009

Tessier E, Garnier C, Mullot JU, Lenoble V, Arnaud M, Raynaud M, Mounier S (2011) Study of the spatial and historical distribution of sediment inorganic contamination in the Toulon bay (France). Mar Pollut Bull 62:2075–2086

Thompson PA, Kurias J, Mihok S (2005) Derivation and use of sediment quality guidelines for ecological risk assessment of metals and radionuclides released to the environment from uranium mining and milling activities in Canada. Environ Monit Assess 110:71–85

USEPA (2007) Microwave assisted acid digestion of sediments, sludges, soils, and oils. Method 3051A. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, US Government Printing Office, Washington, DC

Varol M, Sen B (2012) Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey. Catena 92:1–10

Wenning R, Batley G, Ingersoll C, Moore D (2005) Use of sediment quality guidelines and related tools for the assessment of contaminated sediments. Society of Environmental Toxicology and Chemistry (SETAC) Press, USA

Yu R, Hu G, Wang L (2010) Speciation and ecological risk of heavy metals in intertidal sediments of Quanzhou Bay, China. Environ Monit Assess 163:241–252