



Distribution, correlation and risk assessment of selected metals in urban soils from Islamabad, Pakistan

Javed Iqbal, Munir H. Shah*

Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

ARTICLE INFO

Article history:

Received 19 January 2011

Received in revised form 25 May 2011

Accepted 31 May 2011

Available online 15 June 2011

Keywords:

Soil

Risk assessment

Metal

Multivariate analysis

Pakistan

ABSTRACT

Urban soil samples were analyzed for Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Pb, Sr and Zn by atomic absorption spectrophotometric method. Multivariate statistical approach was used to study the apportionment of selected metals in the soil samples during summer and winter. The degree of contamination along with the geoaccumulation index, enrichment factor and contamination factor was also evaluated. In water-extract of the soil samples, relatively higher levels were noted for Na, Ca, K, Fe, Mg, and Pb with average concentrations of 56.38, 33.82, 12.53, 7.127, 5.994, and 1.045 mg/kg during summer, while the mean metal levels during winter were 76.45, 38.05, 3.928, 0.627, 8.726, and 0.878 mg/kg, respectively. In case of acid-extract of the soils, Ca, Fe, Mg, Na, K, Mn and Sr were found at 27,531, 12,784, 2769, 999.9, 737.9, 393.5, and 115.1 mg/kg, during summer and 23,386, 3958, 3206, 254.6, 1511, 453.6, and 53.30 mg/kg, during winter, respectively. Most of the metals showed random distribution with diverse correlations in both seasons. Principal component analysis and cluster analysis revealed significant anthropogenic intrusions of Cd, Pb, Co, Cr, Cu, Li, Zn and Na in the soils. Geoaccumulation indices and contamination factors indicated moderate to heavy contamination for Pb and Cd in the soils, while enrichment factor exhibited significant enrichment ($EF > 5$) of Cd, Pb, Ca, Co, Li, Mn and Zn by anthropogenic activities. Overall, on the average basis, considerable degree of contamination ($C_{deg} > 16$) was observed in both seasons, although it was higher in winter. Present metal levels were also compared with those reported from other areas around the world.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Soil is the most important environmental component because it is not only a geochemical sink for contaminants, but also acts as a natural buffer by controlling the transport of chemical elements and substances to the atmosphere, hydrosphere and biosphere [1]. The anthropogenic impact on the soil has been very broad and complex, which may lead to the irreversible changes by disturbing the natural balance of the ecosystem that has been formed over a long period of time. These changes most often lead to a degradation of the natural environment. Among the anthropogenic contaminants, heavy metals are of major significance because of their persistence and toxicity [2]. Soil can behave as a sink for heavy metals resulting from the deposition of particles emitted by urban and industrial activities, vehicle exhausts and agricultural practices [3–5]. Increased inputs of the metals and synthetic chemicals in the terrestrial environment due to rapid industrialization coupled with inadequate environmental management in the developing country, has led to large-scale pollution of the environment. Elevated

concentrations of trace elements can have adverse effects on soil biology and functions [6–8]. Soil pollution can have implications in phytotoxicity at high concentrations and result in the transfer of heavy metals to the human diet through food chain, which pose a significant risk to the human health [1,2,9–12]. Measurement of total metal contents is a poor indicator of metal leachability, solubility, bioavailability, mobility and toxicity, therefore, estimation of the available/soluble fraction is of prime importance [13–16]. Leaching of the metals from soil into water, and their availability to the plants and other organisms depends upon the soluble/exchangeable fraction of these metals [14,17–18], which would help to assess the potential for mobilization of the metals at contaminated sites and their availability to other organisms [15]. Recent studies highlighted the importance of metal contamination of soils in ecologically sensitive areas, which are the source sites of drinking water [7,19]. Analysis of the metal contents in soil is, therefore, critical for formulating the policies aimed at reducing the metal inputs and maintaining and/or improving the soil functions and water quality of the reservoir.

The present study is carried out as a preliminary survey of soil contamination around Rawal Lake, Islamabad, Pakistan. The study is the first of its kind in the area and it is based on some previous reports manifesting significant anthropogenic pollution of the lake

* Corresponding author. Tel.: +92 51 90642137; fax: +92 51 90642241.

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

water and associated fauna [20–22]. The main objective of the study was the evaluation of the distribution and covariation of total and soluble fractions of selected metals (Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Pb, Sr and Zn) in soil around the Lake and then to gauge their anthropogenic inputs using multivariate statistical tools. The potential ecological risk index, which may be used as a diagnostic tool for determining the degree of pollution in the soil, was also assessed using the geoaccumulation index (I_{geo}), enrichment factor (EF), contamination factor (C_f) and degrees of contamination (C_{deg}). It is anticipated that the study would provide a baseline data regarding the distribution and accumulation of the selected metals in the soil and would help to reduce the contamination around the water reservoir by identifying the major pollution sources. It would also be helpful in designing the pollution abatement strategy to control the emission and spread of the pollutants in the environment.

2. Materials and methods

2.1. Study area

The study was conducted around the Rawal Lake, Islamabad, Pakistan (Fig. 1). The Lake is an artificial reservoir that provides the water needs for the cities of Rawalpindi and Islamabad. This Lake covers an area of 8.8 km² (longitude: 73°07'E and latitude: 33°41'N). Its drinking water supply capacity is 19.5 million gallons/day for Rawalpindi and 2.5 million gallons/day for Islamabad. Rawal Lake is located within an isolated section of the Margalla Hills National Park in an area that forms the northeast part of the Pothohar Plateau. The area around the Lake has been planted with flowering trees and laid out with gardens, picnic spots, and secluded paths. The metals in the soils can reach to the aquatic ecosystems by erosion and runoff from soil. Protection of the soil quality around the Lake is of great importance for safeguarding the water quality in the reservoir. Untreated urban wastewater effluents, runoff from poultry farms and pollutants released during the recreational use of motorboats are among the major contamination sources [23–24].

2.2. Sample collection and preservation

Triplicate surface soil samples around the lake were collected in summer and winter 2008. The composite surface soil samples (0–10 cm deep top layer) were collected in pre-cleaned Ziploc polythene bags, which were kept in airtight large plastic containers. Any foreign material/debris from the soil samples was manually removed during the sample collection. The soil samples were oven dried, grounded, homogenized and sealed in clean polythene bags and then stored in a refrigerator [25]. The soils in the area are mostly classified as limestone and sandstone [26,27].

2.3. Sample preparation and analysis

The soil samples were processed to assess the soluble/extractable and total concentrations of the metals. A single-step extraction procedure, using deionized water, was applied to the soil samples at room temperature [16,28]. One aliquot of 20 g of each solid sample was added to 40 mL of deionized water. The extractions were performed in pre-cleaned glass vessels by shaking, in an auto-shaker at 240 vibrations per minute for 2 h. Three replicate extractions were performed for each sample. The final extract was separated from the solid residue through filtration using a fine filter paper [15,25].

To estimate the total metal contents, 1–2 g dried soil sample was digested in a microwave system using acid mixture (9-mL

HNO₃ + 3-mL HCl) [29]. For each digestion, a blank was also prepared with the same amount of acids without soil sample. The digested samples were then filtered through the fine filters and made up to 50 mL with deionized water and stored at 4 °C. Selected metals; Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Pb, Sr and Zn in water-extract and acid-extract of the soil samples were analyzed using flame atomic absorption spectrophotometer (Shimadzu AA-670, Japan) under optimum analytical conditions. Calibration line method was used for the quantification of selected metals and the samples were appropriately diluted whenever required [25,30]. Standard reference material was also used to ensure the reliability of the metal data (SRM 2711).

Analytical grade chemicals were used throughout the study without any further purification. To prepare all the reagents and calibration standards, doubly distilled water was used. The metal standards were prepared from stock solution of 1000 mg/L by successive dilutions. The glassware was washed with dilute nitric acid followed by several portions of distilled water. All the measurements were made in triplicate.

2.4. Statistical analysis

Statistical methods were applied to process the analytical data in terms of its distribution and correlation among the studied parameters. STATISTICA software was used for statistical analyses of the metal data [31]. Basic statistical parameters such as range, mean, median, standard deviation (SD), standard error (SE) and skewness were computed along with correlation analysis, while multivariate statistics in terms of principal component analysis (PCA) and cluster analysis (CA) were also carried out [32–35]. The PCA was carried using varimax normalized rotation on the dataset and the CA was applied to the standardized matrix of samples, using Ward's method. PCA is mainly used for data reduction and it aims at finding a few components that explain the major variation within the data. Each component is a weighted, linear combination of the original variables. CA organizes a set of variables into two or more mutually exclusive unknown groups/clusters based on combination of internal variables. The purpose of CA is to discover a system of organizing variables where each cluster shares properties in common. Thus, it is cognitively easier to predict mutual properties based on an overall group membership.

The index of geoaccumulation (I_{geo}) enables the assessment of contamination by comparing the current and pre-industrial concentrations [36]. It can also be applied to the assessment of soil contamination. It is computed using the following Eq. (1):

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (1)$$

where C_n is the mean concentration of the element in the examined soil and B_n is the geochemical background value in the crust. The factor 1.5 was introduced to minimize the effect of possible variations in the background values which may be attributed to lithogenic variations. In the present paper, the modified calculation based on the equation given by Loska et al. [37] was applied, where C_n denoted the concentration of a given element in the examined soil and B_n denoted the concentration of the element in the earth's crust [38]. Here the focus is between the concentration obtained and the concentration of elements in the earth's crust, because chemical composition of soil is related to the one of the crust.

The extent of metal pollution in the soil was also assessed using enrichment factor (EF) which represents the contamination level in the soil and is a good tool to differentiate between the anthropogenic and natural sources of the metals [39–41]. EFs are usually taken as double ratios of the target metal and a reference metal in the examined soil and earth crust. Usually, Al, Mg, Ca, Mn and Fe are

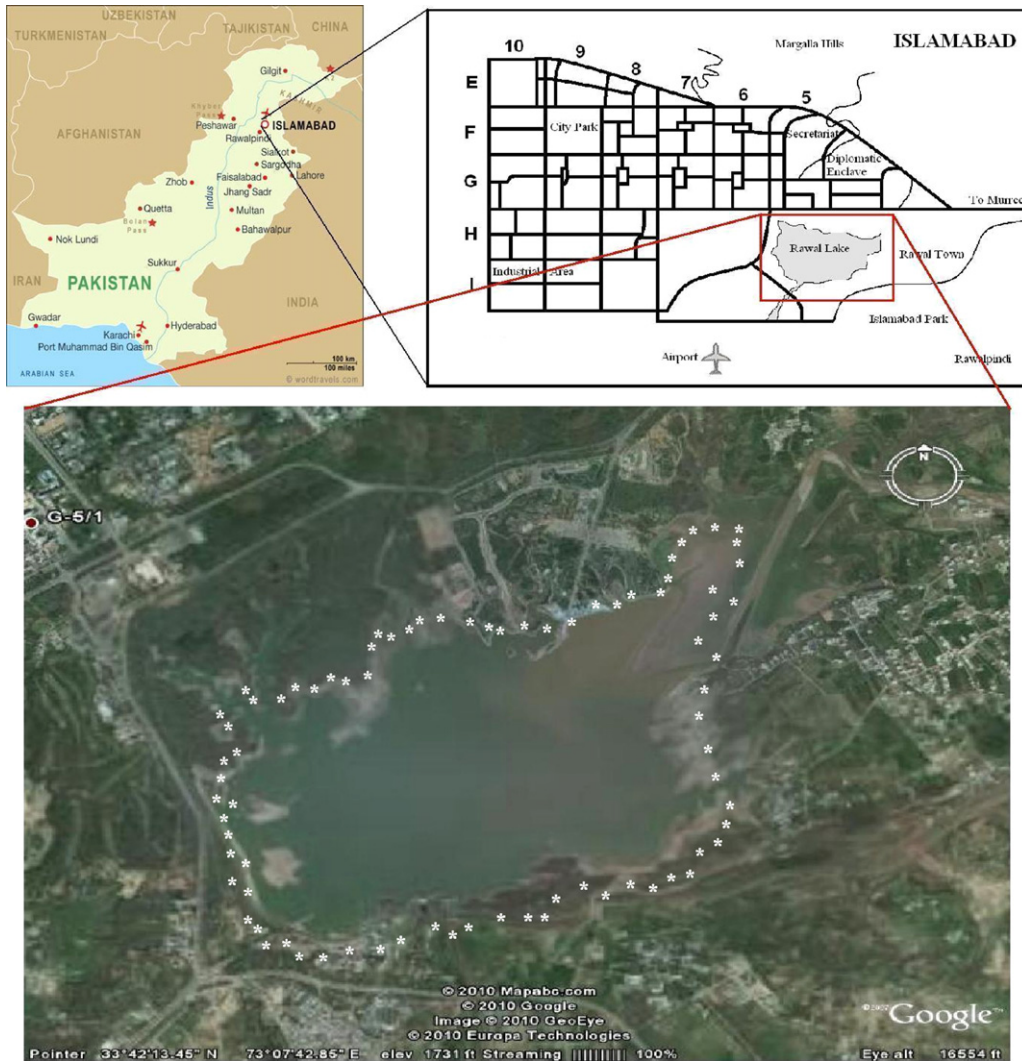


Fig. 1. Location of the sampling points (*) in the study area.

used as the reference. In present study, EFs were calculated using Fe as the reference, using the relationship:

$$EF = \frac{[X/Fe]_{\text{sample}}}{[X/Fe]_{\text{crust}}} \quad (2)$$

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

The assessment of soil contamination was also carried out using the contamination factor (C_f) and degree of contamination (C_{deg}). In the version suggested by Hakanson [42], an assessment of soil contamination was carried by using the relationship:

$$C_f^i = \frac{C_i}{C_n^i} \quad (3)$$

here C_i and C_n^i refer to the mean concentration of a pollutant in the examined site and the pre-industrial soil, respectively. The C_f is the single element index. The sum of contamination factors for all elements examined represents the contamination degree (C_{deg}) of the environment which is calculated as under:

$$C_{\text{deg}} = \sum_{i=1}^{i=n} C_f^i \quad (4)$$

In this study, a modification of the factor as applied by Loska et al. [37] that used the concentration of the elements in the earth's crust as a reference value was also used similar to other indices.

3. Results and discussion

The physicochemical parameters pertaining to the water-extract of the soil samples are given in Table 1. The soils were found to be slightly basic showing mean pH values of 7.690 and 8.108 during summer and winter, respectively. Electrical conductivity (EC) values were significantly higher during winter (383.0 $\mu\text{S}/\text{cm}$) compared to the summer (249.6 $\mu\text{S}/\text{cm}$), which may be associated with the climatic variations as most of the precipitation is observed during summer while winter mostly remains dry [43]. Consequently, the soluble ions may be leached out during summer, thus exhibiting relatively lower EC values. Exactly a similar behavior was shown by total dissolved solids (TDS); the average levels during summer (124.3 mg/L) were significantly lower than winter (191.3 mg/L). The moisture contents were marginally higher during summer, but the difference was not significant.

The statistical summary of the distribution parameters for the selected metals in water-extract of the soil samples during summer and winter is given in Table 2, whereas, their quartile distribution is shown as Box and Whisker plot in Fig. 2. Dur-

Table 1
Statistical summary of physicochemical parameters in water-extract of the soil samples ($n = 80$).

	Min	Max	Mean	Median	SD
Summer					
pH	7.090	8.300	7.690	7.675	0.302
EC ($\mu\text{S}/\text{cm}$)	92.50	830.0	249.6	191.7	147.9
TDS (mg/L)	45.90	415.0	124.3	95.60	73.96
Moisture content (%)	7.220	19.22	13.14	13.48	2.924
Winter					
pH	7.650	8.300	8.108	8.150	0.159
EC ($\mu\text{S}/\text{cm}$)	151.0	2634	383.0	267.5	447.2
TDS (mg/L)	75.00	1322	191.3	133.3	224.5
Moisture content (%)	7.07	18.53	11.96	11.83	3.142

ing summer, considerably elevated mean levels were shown by Na (56.38 mg/kg), Ca (33.82 mg/kg), K (12.53 mg/kg), Fe (7.127 mg/kg), Mg (5.994 mg/kg) and Pb (1.045 mg/kg), while, during winter, Na (76.45 mg/kg), Ca (38.05 mg/kg), Mg (8.726 mg/kg) and K (3.928 mg/kg) revealed dominant contributions. The quartile distribution showed random and broad distribution for most of the metals in the water-extract of the soils; the dispersion was relatively higher during summer. On the average basis in water-extract of the soils during summer, the metal levels showed following order; Na > Ca > K > Fe > Mg > Pb > Sr > Cr > Zn > Co > Mn > Cu > Li > Cd, whereas, during winter the decreasing concentration order was; Na > Ca > Mg > K > Pb > Fe > Sr > Co > Cr > Cu > Cd > Zn > Mn > Li. The average water soluble concentrations of Fe, K, Li, Zn, Cr and Pb were noticeably higher during summer compared with the winter. The elevated levels of these metals are associated with most of the anthropogenic activities, particularly the recreational and agricultural activities, which are at the peak during summer when the water level is highest in the Lake. However, during winter,

these anthropogenic activities are very limited and hence the contribution of the metals is considerably diminished. Most of the lithogenic elements (Ca, Mg, Na, Sr, etc.) manifested higher levels during winter which are mainly due to the dry conditions/scarcie precipitation as explained earlier.

The distribution of selected metals in the acid-extract of the soil samples during summer and winter are given in Table 3, while their quartile distribution is shown in Fig. 3. The data showed that Ca (27,531 mg/kg), Fe (12,784 mg/kg) and Mg (2769 mg/kg) were among the dominant metals in the acid-extract of the soil samples during summer, followed by Na (999.9 mg/kg) and K (737.9 mg/kg), while Mn (393.5 mg/kg), Sr (115.1 mg/kg) and Pb (38.25 mg/kg) exhibited relatively low concentrations. The acid-extract of soil samples during summer were found to have lowest levels of Cu (10.28 mg/kg) and Cd (1.568 mg/kg), while the average levels of Zn, Cr, Li and Co were slightly higher. Among the selected metals during summer, Na, Mn and Cd showed almost equivalent mean and median levels, associated with minimum skewness values indicat-

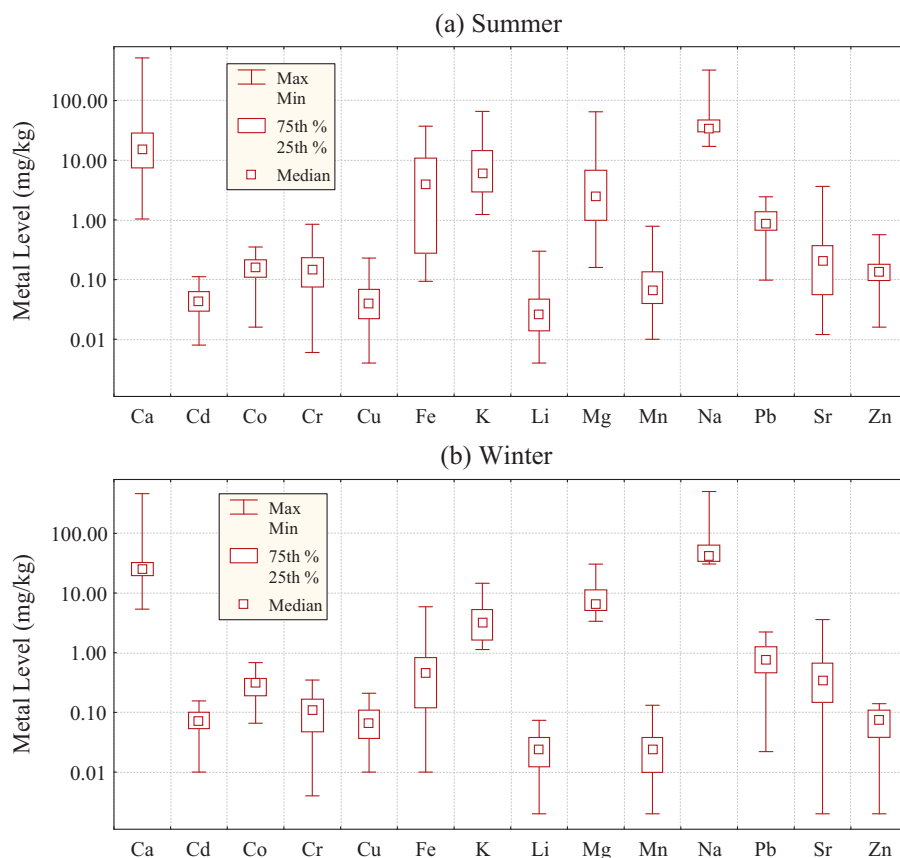


Fig. 2. Quartile distribution of selected metals in water-extract of the soil samples.

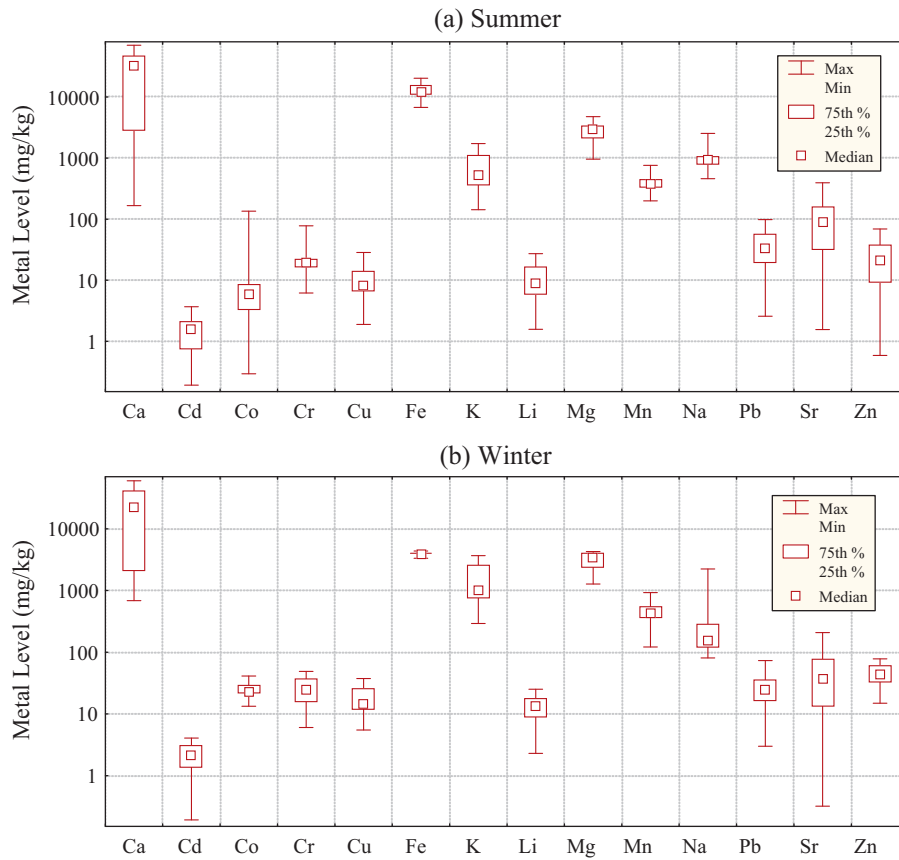


Fig. 3. Quartile distribution of selected metals in acid-extract of the soil samples.

ing almost normal distribution of these metals. Rest of the metals showed somewhat dissimilar mean and median levels, thus reflecting relatively non-Gaussian distribution during summer. Highest dispersion in terms of elevated SD and SE values during summer was exhibited by Ca, Fe, Mg, K, Na, Mn and Sr. The quartile distribution of metal concentrations in acid-extract is shown in Fig. 3a, where Fe, Mg, Na, and Mn revealed very narrow distribution while, rest of the metals mostly showed random and broad distribution.

The counterpart data during winter (Table 3) showed that on the average basis, Ca (23,386 mg/kg), Fe (3958 mg/kg), Mg (3206 mg/kg) and K (1511 mg/kg) were among the dominant metals in acid-extract, followed by Mn (453.6 mg/kg), Na (254.6 mg/kg), Sr (53.30 mg/kg) and Zn (45.03 mg/kg). Among the selected metals, Cu, Li and Cd showed the lowest mean concentrations. Among the selected metals in acid-extract of the soils during winter, Li, Cd and Fe manifested almost comparable mean and median concentrations, associated with lowest asymmetry indicating more or less normal distribution of these metals. Rest of the metals showed relatively divergent mean and median levels, thus reflecting random distribution during winter. The quartile distribution of metal concentrations in acid-extract during winter is shown in Fig. 3b, where Fe and Mg revealed very narrow distribution with overlapping lower and upper quartiles. Relatively symmetric distribution for Zn, Pb and Cr was observed, while, rest of the metals mostly showed random and asymmetric distribution during winter. Most of the selected metals during summer showed relatively higher values of SD and SE than winter, indicating larger dispersion associated with anthropogenic activities. Mean concentration of Fe in the acid-extract of the soil was significantly higher during summer compared to the winter, which is mainly due to the excessive anthropogenic activities around the lake during summer. Similar pattern was also shown by Na, Pb and Sr. Nonetheless, most of the

selected metals (Ca, Mg, Li, Mn, Cd and Cr) showed insignificant seasonal variations. Average levels of K, Zn, Co and Cu were considerably higher during winter. The quartile distribution of metal levels during summer and winter (Fig. 3) indicated comparatively narrow distribution for Fe and Mg; however, Ca and Sr exhibited broad range and predominantly non-Gaussian distribution.

Comparison of leachability of average selected metal levels in water-extract and acid-extract of the soil during summer and winter (Fig. 4) helped to elucidate the extraction efficiencies. Among the selected metals, Na and Cd manifested maximum extraction efficiencies, followed by those of Pb, K, Co and Sr with moderate extraction efficiencies. The extraction efficiency of Na was signif-

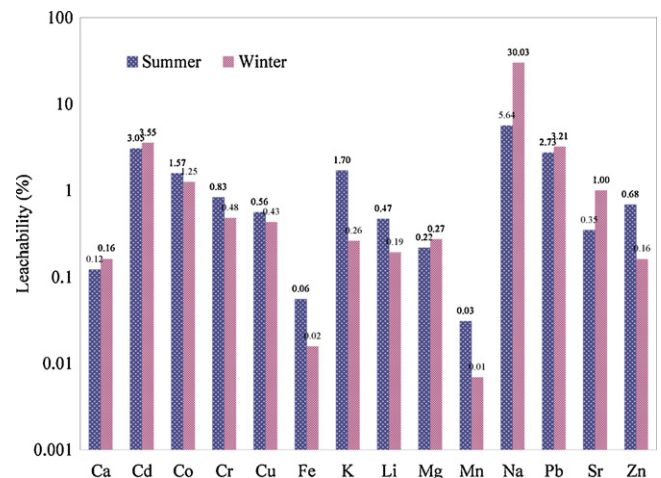


Fig. 4. Leachability of selected metals in water-extract of the soil samples.

Table 2
Statistical parameters for selected metal distribution in water-extract of soil (mg/kg) during summer and winter ($n = 80$).

	Summer							Winter						
	Min	Max	Mean	Median	SD	SE	Skew	Min	Max	Mean	Median	SD	SE	Skew
Ca	1.040	518.0	33.82	15.05	82.02	12.97	5.568	5.384	464.8	38.05	25.38	74.72	12.63	5.800
Cd	0.008	0.112	0.048	0.043	0.026	0.004	0.648	0.010	0.156	0.076	0.072	0.036	0.006	0.312
Co	0.016	0.352	0.162	0.158	0.081	0.013	0.282	0.066	0.684	0.314	0.312	0.159	0.027	0.783
Cr	0.006	0.846	0.175	0.146	0.151	0.024	2.585	0.004	0.350	0.124	0.110	0.090	0.015	0.818
Cu	0.004	0.230	0.057	0.039	0.056	0.010	1.867	0.010	0.210	0.076	0.066	0.051	0.009	0.937
Fe	0.094	37.30	7.127	3.997	9.283	1.468	1.688	0.010	5.894	0.627	0.452	0.985	0.167	4.721
K	1.236	66.02	12.53	6.025	16.43	2.597	2.332	1.134	14.59	3.928	3.178	3.217	0.544	2.065
Li	0.004	0.300	0.051	0.026	0.069	0.012	2.402	0.002	0.074	0.025	0.024	0.016	0.003	0.758
Mg	0.160	64.88	5.994	2.486	11.40	1.803	4.194	3.374	30.50	8.726	6.414	6.038	1.021	2.065
Mn	0.010	0.784	0.122	0.065	0.151	0.025	2.743	0.002	0.132	0.031	0.024	0.031	0.005	1.861
Na	17.12	324.8	56.38	33.75	64.17	10.15	3.232	30.68	502.6	76.45	42.46	88.57	14.97	3.688
Pb	0.098	2.444	1.045	0.851	0.586	0.093	0.682	0.022	2.228	0.878	0.764	0.570	0.096	0.337
Sr	0.012	3.666	0.398	0.203	0.711	0.122	3.739	0.002	3.590	0.533	0.338	0.682	0.115	3.198
Zn	0.016	0.566	0.163	0.136	0.116	0.018	2.130	0.002	0.140	0.073	0.074	0.039	0.007	-0.319

Table 3
Statistical parameters for selected metal distribution in acid-extract of the soil (mg/kg) during summer and winter ($n = 80$).

	Summer							Winter						
	Min	Max	Mean	Median	SD	SE	Skew	Min	Max	Mean	Median	SD	SE	Skew
Ca	166.7	70,366	27,531	32,299	21,905	3464	0.009	685.7	59,983	23,386	22,527	19,358	3272	0.262
Cd	0.192	3.678	1.568	1.542	0.950	0.150	0.429	0.192	4.057	2.132	2.155	0.976	0.165	-0.196
Co	0.295	135.0	10.34	5.821	21.84	3.591	5.458	13.29	41.09	25.08	22.81	5.548	0.938	0.822
Cr	6.181	77.67	21.01	19.51	10.36	1.638	4.322	6.028	48.95	25.73	24.73	11.77	1.989	0.208
Cu	1.894	28.44	10.28	8.058	5.925	0.937	1.132	5.481	37.57	17.77	14.28	8.050	1.361	0.735
Fe	6771	20,293	12,784	12,265	3129	494.7	0.270	3327	4386	3958	3941	210.5	35.58	-0.494
K	143.1	1732	737.9	521.8	450.7	71.26	0.686	291.7	3675	1511	999.2	965.0	163.1	0.701
Li	1.573	27.34	10.87	8.841	6.575	1.053	0.596	2.292	25.11	13.27	13.28	5.234	0.885	0.261
Mg	961.5	4769	2769	2980	767.6	121.4	-0.869	1275	4280	3206	3452	892.6	150.9	-0.571
Mn	199.2	760.6	393.5	382.8	118.9	18.79	1.041	121.8	927.0	453.6	422.1	167.1	28.25	0.698
Na	459.7	2529	999.9	920.7	331.7	52.44	2.754	80.87	2240	254.6	154.0	359.8	60.82	5.222
Pb	2.579	98.40	38.25	32.94	24.03	3.799	0.581	2.986	73.02	27.35	24.17	17.35	2.932	1.015
Sr	1.558	394.0	115.1	88.45	110.4	18.93	1.256	0.320	208.4	53.30	36.28	59.72	10.10	1.621
Zn	0.587	69.30	23.83	20.77	17.06	2.698	0.673	14.95	77.90	45.03	43.80	14.99	2.534	0.194

Table 4Correlation coefficient (r)^a matrix of selected metals in water-extract of the soil during summer (below the diagonal) and winter (above the diagonal) ($n = 80$).

	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Pb	Sr	Zn
Ca	1	-0.088	-0.074	-0.086	-0.116	-0.069	-0.014	0.002	0.823	-0.276	-0.091	-0.173	0.789	0.074
Cd	0.121	1	0.174	-0.501	-0.551	-0.127	-0.573	-0.613	-0.306	-0.348	-0.218	-0.048	-0.077	-0.568
Co	0.310	-0.131	1	0.018	0.031	-0.012	-0.123	-0.105	-0.045	-0.247	-0.115	-0.170	-0.102	-0.111
Cr	0.003	0.073	0.360	1	0.144	0.123	-0.002	0.284	0.116	0.038	-0.054	0.394	-0.018	0.366
Cu	-0.026	0.302	0.316	0.532	1	0.445	0.797	0.889	0.249	0.675	0.345	-0.208	-0.189	0.837
Fe	-0.232	0.112	0.193	0.796	0.589	1	0.419	0.666	0.332	0.489	0.121	-0.211	-0.211	0.603
K	-0.166	-0.019	0.251	0.744	0.659	0.880	1	0.773	0.340	0.641	0.417	-0.337	-0.153	0.656
Li	-0.188	-0.122	0.256	0.750	0.568	0.878	0.935	1	0.423	0.638	0.337	-0.228	-0.107	0.931
Mg	0.884	-0.041	0.284	-0.095	-0.128	-0.299	-0.180	-0.182	1	0.070	-0.044	-0.289	0.541	0.469
Mn	-0.176	0.049	-0.043	0.475	0.383	0.793	0.639	0.721	-0.219	1	0.355	-0.299	-0.283	0.634
Na	0.637	0.014	0.214	0.108	0.072	-0.070	0.036	0.094	0.688	-0.051	1	-0.107	-0.069	0.357
Pb	-0.234	0.072	0.262	0.276	0.245	0.267	0.180	0.099	-0.219	0.107	-0.123	1	0.036	-0.231
Sr	0.584	-0.173	0.208	-0.171	-0.192	-0.275	-0.210	-0.183	0.821	-0.176	0.374	-0.260	1	-0.038
Zn	-0.201	-0.110	0.200	0.728	0.562	0.855	0.865	0.886	-0.231	0.688	0.109	0.205	-0.253	1

^a r -Values >0.330 of <-0.330 are significant at $p < 0.01$.**Table 5**Correlation coefficient (r)^a matrix of selected metals in acid-extract of the soil during summer (below the diagonal) and winter (above the diagonal) ($n = 80$).

	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Pb	Sr	Zn
Ca	1	0.117	-0.007	0.009	0.051	-0.031	0.215	-0.068	0.481	-0.204	-0.006	0.106	0.806	0.300
Cd	0.068	1	0.016	0.040	-0.120	-0.018	-0.012	0.018	-0.061	0.199	-0.152	0.128	0.049	0.352
Co	-0.236	-0.166	1	0.248	0.439	0.134	0.008	0.080	-0.284	-0.264	-0.080	-0.124	-0.073	0.065
Cr	0.316	-0.176	-0.066	1	0.331	0.112	-0.073	0.041	-0.206	0.065	-0.132	0.053	0.030	-0.014
Cu	-0.081	0.220	0.043	-0.027	1	-0.076	0.003	-0.141	-0.131	-0.205	-0.030	0.110	-0.014	-0.116
Fe	0.134	0.153	0.027	0.171	0.447	1	0.555	0.082	-0.103	0.368	0.241	-0.030	-0.016	0.020
K	-0.062	0.107	-0.007	-0.112	0.827	0.458	1	-0.122	0.308	0.111	0.313	-0.133	0.193	0.211
Li	0.033	0.455	-0.072	-0.013	0.393	0.227	0.351	1	0.033	-0.098	0.052	-0.134	-0.006	0.022
Mg	0.671	0.218	-0.302	0.120	0.320	0.382	0.364	0.327	1	-0.187	0.549	-0.212	0.622	0.308
Mn	0.161	0.120	0.138	0.332	0.118	0.508	0.204	0.198	0.187	1	0.074	-0.311	-0.246	-0.214
Na	-0.338	0.074	-0.098	-0.084	0.148	0.363	0.259	0.012	-0.083	0.221	1	-0.448	-0.103	0.237
Pb	0.007	-0.060	0.203	-0.186	-0.087	-0.208	-0.047	0.021	0.069	-0.076	0.024	1	0.140	-0.207
Sr	0.570	0.098	-0.207	-0.097	-0.129	0.276	-0.077	-0.136	0.570	-0.136	-0.007	-0.112	1	0.229
Zn	0.285	0.178	0.045	-0.068	0.533	0.433	0.594	0.564	0.496	0.438	0.146	-0.042	0.115	1

^a r -Values >0.330 of <-0.330 are significant at $p < 0.01$.

icantly higher during winter, which is mostly due to the climatic variation during summer and winter. As explained earlier [43], most of the precipitation is observed during summer which partially remove the soluble metal contents from the soil, whereas, winter mostly remains dry thereby accumulating the deposited metal contents in the soil. Another interesting finding was relatively higher extraction efficiency of Pb, which is believed to be one of the least mobile element in the earth crust but its anthropogenic contribution is mostly water soluble [15,16]. Hence, the present study revealed significant anthropogenic contribution of Pb in soils. On the other hand, Ca, Mn and Fe showed the least efficiencies. Since metal solubility is related to metal bioavailability, extractable metal levels may correspond to the bioavailable metal concentrations [44]. Therefore, Na, K, Pb, Cd and Co were most bioavailable in the soil samples compared to the other metals. Among the selected metals, Ca, Cd, Mg, Na, Pb and Sr were relatively more leachable in winter, while, rest of the metals revealed opposite behavior.

Multivariate analysis by means of PCA/CA and correlation matrixes can shed more light and help understanding these data. Inter-element relationships can provide interesting information on element sources and pathways. The correlation data of water-extract and acid-extract of the soils are given in Tables 4 and 5, respectively. The data showed strong relationships among Ca, Mg, Na and Sr, thus indicating close association of these metals in the soluble fraction of the soil during summer, while, these metals exhibited significantly negative correlations with most of the metals (Cr, Fe, K, Li, Zn, Cu and Mn). The correlation data of water-extract of the soils during winter revealed strong correlation among Ca, Mg and Sr, indicating probably common origin of these metals. Some of the metals revealed inverse relationships, such as, Cd, Co and Pb with Cr, Cu, Fe, K, Li, Mg, Mn, Na, Pb, Sr and Zn. These associations can be more clearly assessed through multivariate analysis.

The metal data of acid-extract of the soil during summer (Table 5) showed significant and strong correlations among Ca, Mg, and Sr, manifesting an apparent common source of these metals. Another group of the metals comprising of Zn, Cu, K, Li, Mn and Fe was also identified based on mutual correlations. Among the selected metals, Cd, Co and Cr were inversely correlated with most of the metals, thus reflecting their diverse variability in acid-extract of the soil samples during summer. The counterpart data of acid-extract of the soil during winter showed significant and strong correlations among Ca, Mg, Sr and Na, manifesting a mutual origin of the metals. Another group of selected metals comprising of K, Cu and Mn was also identified based on common relationships. The sources of these metals would further be investigated by multivariate statistics. The multivariate PCA and CA were employed in order to understand the complex nature of the relationships and apportionment among the metals in soil samples.

The PC loadings of selected metals for acid-extract of the soil during summer and winter are shown in Table 6, whereas, the corresponding CA of selected metals are shown in the form of dendrogram in Fig. 5. In case of acid-extract of the soil during summer, five principal components (PCs) were obtained with eigen values greater than 1, together explaining more than 74% variance of the data. First PC exhibited elevated loadings of Cu, K and Zn which also constituted a strong cluster, mostly coming from both natural and anthropogenic sources. PC 2 indicated significant loadings in favor of Ca, Mg and Sr along with a strong cluster in CA. These metals were believed to be contributed by the lithogenic source. Third PC revealed higher contributions of Cd, Co, Li and Na, also supported by a common cluster of these metals, indicating anthropogenic intrusion in the soil samples. PC 4 showed similar behavior of Cr–Fe–Mn, indicating their natural origin. The last PC was composed of Pb and Na, generally contributed by the anthropogenic source. CA was in total agreement with the PCA results. Nevertheless, in case of acid-extract of the soil during winter, four principal

components (PCs) were obtained with eigen values greater than 1, together explaining more than 77% variance of the data. First PC exhibited elevated loadings of Na, Cu, Fe, K, Li, Mn and Zn which also constitute a strong cluster, contributed by mixed source. PC 2 indicated significant loadings in favor of Ca, Mg and Sr along with a strong cluster in CA. These metals were believed to be contributed by the lithogenic sources. PC 3 and 4 revealed higher contributions of Cr–Pb and Cd–Co, respectively. The CA also demonstrates shared clusters of Pb–Cr and Cd–Co, respectively, indicating anthropogenic interferences in the soil samples.

The contamination levels of selected metals were also assessed by using geoaccumulation index (I_{geo}) (Table 7). It is the quantitative measure of the pollution index in the soils. The contamination level is assessed by comparing the current and preindustrial concentrations of the metals in soils. Any increase in the current levels is envisaged to be anthropogenic in nature. The natural fluctuations in the metal contents of the soils are countered by a constant factor 1.5. Fig. 6a demonstrates the minimum, mean and maximum I_{geo} values of selected metals in acid-extract of the soil during summer and winter. Among the metals, the mean I_{geo} values of Pb and Cd indicated moderately to heavily contamination, respectively. Rest of metals (Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Sr and Zn) revealed practically un-contamination to the soils. The average I_{geo} values for Cd showed that the soil was moderately to heavily contaminated during summer and heavily contaminated in the winter. Rest of the metals showed almost similar behaviors during both season. During summer, the highest I_{geo} values for Co, Pb and Cd classified the soil as moderately contaminated, moderately to heavily contaminated and heavily to extremely contaminated, respectively, whereas during winter, the values for Co, Pb and Cd categorized the soil as uncontaminated to moderately contaminated, moderately contaminated and heavily to extremely contaminated, respectively.

The geochemical normalization was also carried out to calculate enrichment factor (EF) and to assess the anthropogenic intrusions of the metals in soils [39–41]. EF is based on the standardization of a measured metal against a reference one, which is characterized by low occurrence variability. The ratio of the measured element and the reference are compared for the estimated soil sample and preindustrial concentrations and any increase in the current ratio is linked with anthropogenic intrusion. In the study, the standardization was obtained using Fe as the reference metal, because it is associated with fine solid surfaces; its geochemistry is similar to that of many metals; and its natural concentration tends to be uniform. EF values were interpreted as suggested by Sutherland [45]. Fig. 6b demonstrates the minimum, mean and maximum EF values of the selected metals in acid-extract of the soil during summer and winter. During summer, the mean EF values of Cd and Pb were greater than 40 and 10, respectively; that of Ca and Li were between 2 and 3; and that of rest metals (Co, Cr, Cu, K, Mg, Mn, Na, Sr and Zn) were less than 2. The elements, with the EFs higher than 10 were considered to be mainly anthropogenic in origin. The highest EF values for Co, Pb and Cd were 14.98, 19.50 and 68.02, respectively, indicating that these metal were highly enriched in the soil. During winter, the mean EF values of Cd and Pb were greater than 200 and 25, respectively; that of Ca, Co, Li, Mn and Zn; that of Cr, Cu and Sr were between 2 and 5; and that of K, Mg and Na were less than 2. The highest EF values for Co, Pb and Cd were 21.10, 66.96 and 347.2, respectively, indicating that Cd and Pb were extremely enriched in the soil. Overall, the mean EF values of Pb classified the soil as significantly enriched during summer and very highly enriched during winter, whereas, that of Cd classified the soil as extremely enriched in both seasons.

The assessment of the soil based on the degree of contamination (C_{deg}) was also carried out as suggested by Hakanson [37,42]. It is a cumulative index based on the contamination by each measured

Table 6
Principal component loadings of selected metals in acid extract of the soil samples.

	Summer					Winter			
	PC 1	PC 2	PC 3	PC 4	PC 5	PC 1	PC 2	PC 3	PC 4
Eigen value	3.716	2.522	1.656	1.440	1.148	5.285	2.583	1.701	1.212
% total variance	26.54	18.01	11.83	10.29	8.198	37.75	18.45	12.15	8.660
% cumulative variance	26.54	44.56	56.38	66.67	74.87	37.75	56.20	68.35	77.01
Ca	-0.093	0.793	0.008	0.278	-0.354	0.059	0.970	-0.094	0.000
Cd	0.110	0.157	0.766	0.010	0.048	0.577	-0.189	-0.516	0.263
Co	-0.081	0.343	0.552	-0.241	-0.450	0.002	-0.103	-0.116	0.791
Cr	-0.193	0.014	-0.153	0.626	-0.540	-0.227	0.012	0.874	0.168
Cu	0.909	-0.024	0.030	-0.014	-0.081	0.901	0.068	-0.042	0.080
Fe	0.403	0.423	-0.006	0.615	0.049	0.693	0.032	0.068	-0.250
K	0.914	0.010	0.039	0.013	-0.005	0.833	-0.029	0.131	0.261
Li	0.486	-0.115	0.545	0.185	-0.081	0.956	-0.080	-0.131	0.059
Mg	0.264	0.798	0.171	0.213	-0.090	-0.401	0.857	-0.021	0.131
Mn	0.155	0.025	0.157	0.905	0.066	0.750	0.247	0.142	0.297
Na	0.041	-0.196	0.644	0.191	0.544	0.369	0.125	0.159	0.545
Pb	-0.129	-0.036	-0.009	-0.032	0.770	0.368	-0.160	0.733	-0.174
Sr	-0.073	0.880	-0.001	-0.166	0.105	0.213	0.858	0.057	-0.136
Zn	0.719	0.174	0.238	0.340	0.057	0.914	-0.147	-0.170	0.055

element (C_f) in the soils where the current and preindustrial concentrations are compared on one on one basis. It is considered as more appropriate parameter to assess the overall contamination by all measured element in the soils and hence act as a cumulative index. Fig. 6c demonstrates the minimum, mean and maximum contamination factor (C_f) values of the individual metals in acid-extract of the soil during summer and winter. On the basis of the average C_f values of the selected metals in acid-extract, the soil was classified as least contaminated with Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Sr and Zn; moderately contaminated with Pb; and very highly contaminated with Cd during summer. The highest C_f val-

ues for Pb and Cd were 24.52 and 7.029, respectively, indicating that the soil was very highly contaminated. However, the soil was classified as low contaminated with Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Sr and Zn; moderately contaminated with Co and Pb; and very highly contaminated with Cd during winter. The highest C_f values for Co, Pb and Cd were 1.643, 5.216 and 27.05, classifying the soil as moderately contaminated, considerably contaminated and very highly contaminated, respectively. Overall, the mean C_f values for Pb classified the soil as moderately contaminated during summer and winter, whereas, that of Cd categorized the soil as very highly contaminated during both the seasons. The mean C_{deg} values for

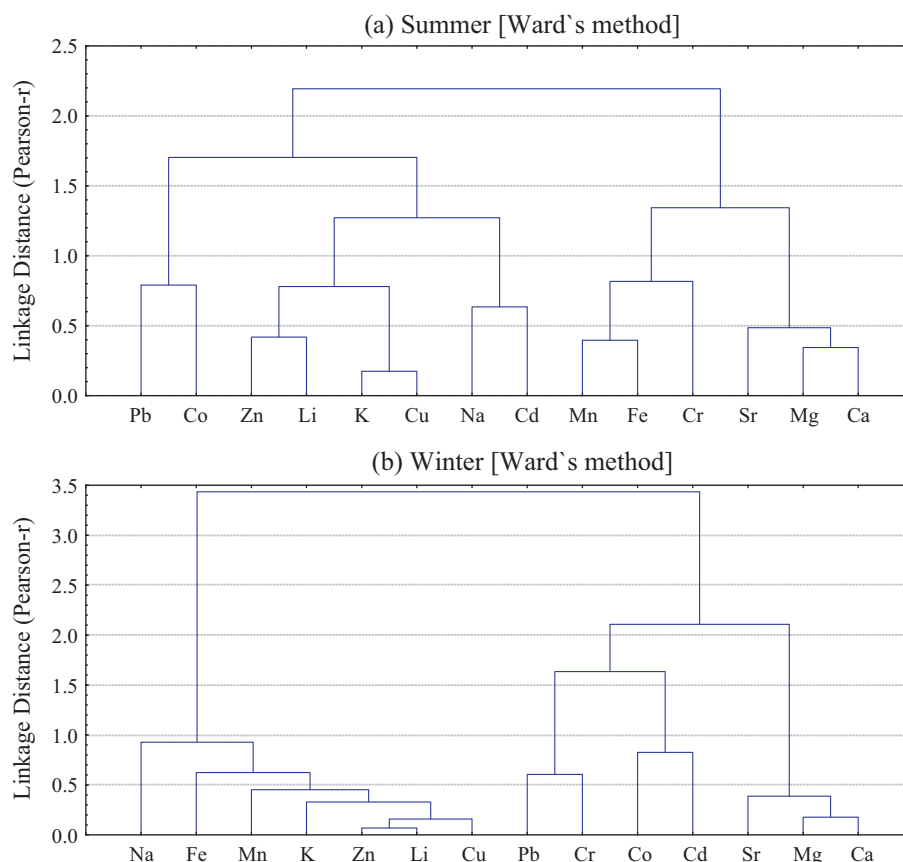


Fig. 5. Cluster analysis of selected metals in acid extract of the soil samples.

Table 7
Description of geoaccumulation index (I_{geo}), enrichment factor (EF), contamination factor (C_f) and degree of contamination (C_{deg}).

Value	Soil quality	Value	Soil quality
$I_{geo} \leq 0$	Practically uncontaminated	$EF < 2$	Deficiency to minimal enrichment
$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated	$2 < EF < 5$	Moderate enrichment
$1 < I_{geo} < 2$	Moderately contaminated	$5 < EF < 20$	Significant enrichment
$2 < I_{geo} < 3$	Moderately to heavily contaminated	$20 < EF < 40$	Very high enrichment
$3 < I_{geo} < 4$	Heavily contaminated	$40 < EF$	Extremely high enrichment
$4 < I_{geo} < 5$	Heavily to extremely contaminated		
$5 < I_{geo}$	Extremely contaminated		
$C_f < 1$	Low contamination factor indicating low contamination	$C_{deg} < 8$	Low degree of contamination
$1 \leq C_f < 3$	Moderate contamination factor	$8 \leq C_{deg} < 16$	Moderate degree of contamination
$3 \leq C_f < 6$	Considerable contamination factor	$16 \leq C_{deg} < 32$	Considerable degree of contamination
$6 \leq C_f$	Very high contamination factor	$32 \leq C_{deg}$	Very high degree of contamination

the metal contents in acid-extract of the soil during summer and winter are 16.67 and 20.50, respectively, indicating considerable degree of contamination. The maximum Cd values during summer and winter are 44.81 and 40.90, respectively, indicating very high contamination.

Present average metal levels in the soils were also compared with those reported from other regions around the world as shown in Table 8. Mean levels of Ca estimated in the present study were higher than most of the reported levels in the Table except Veles, Macedonia [50], whereas, the present Cd levels were comparable to those reported from Himalya, Pakistan [46], Auplia, Italy [49] and Multan Pakistan [34], but less than those reported from Veles, Macedonia [50], and Guwahati, India [47]. Average concentrations of Co in the soils from Multan, Pakistan [34] and Adana, Turkey [19] were significantly higher than the present levels; nonetheless, these levels are either comparable or higher than rest of the sites given in the Table. The Cr levels found in the present study

are considerably higher than those reported from Kasur and Mian Channun, Pakistan [30], Guanting reservoir, China [7] and Central Victoria, Australia [52]. Average Cu contents in the present study were found to be comparable with most of the reported levels, however, lower than those reported from Guwahati, India [47], Apulia, Italy [49] and Veles, Macedonia [50]. Present mean levels of Fe in the soils are although higher than few other studies, are significantly lower than those reported from Yixing, China [48], Galicia, Spain [5], Veles, Macedonia [50], Yocsina, Argentina [51] and Central Victoria, Australia [52]. Mean concentration of K and Li were found to be lower than most of the reported levels in the Table, while, Mg contents were noted to be higher than those reported from Himalya, Pakistan [46], Kasur and Mian Channun, Pakistan [30], and Adana, Turkey [19]. Average levels of Mn in the present study were markedly higher than most of the reported levels, except Galicia, Spain [5] and Veles, Macedonia [50]. Nonetheless, mean levels of Na in the present study were less than most of the reported levels

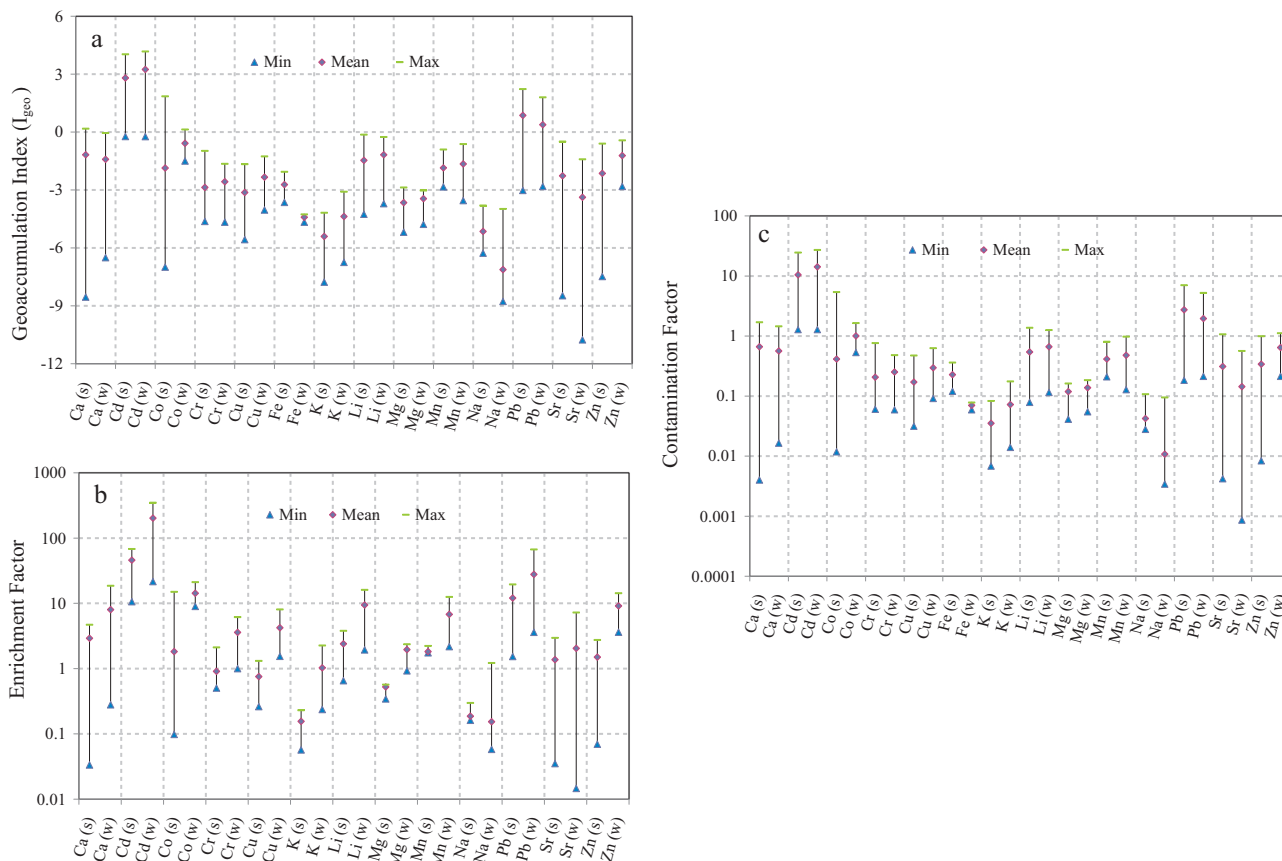


Fig. 6. Summary of (a) geoaccumulation index, (b) enrichment factor and (c) contamination factor for selected metals in acid-extract of the soil samples during summer (s) and winter (w).

Table 8
Average metal concentrations (mg/kg, dry weight) estimated in the present study in comparison with other areas around the world.

Site description	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Pb	Sr	Zn	Ref.
Rawal Lake (Summer)	27,531	1.568	10.34	21.01	10.28	12,784	737.9	10.87	2769	393.5	999.9	38.25	115.1	20.77	a
Rawal Lake (Winter)	23,386	2.132	25.08	25.73	17.77	3958	1511	13.27	3206	453.6	254.6	27.35	53.30	45.30	a
Himalya, Pakistan	3520	1.900	3.490	32.60	18.10	1241	1489	19.60	906.0	343.0	92.30	47.00	-	35.50	[46]
Kasur, Pakistan	1335	0.099	2.794	10.58	-	14.24	610.4	-	137.2	0.743	18,765	1.090	-	0.582	[30]
Mian Channun, Pakistan	800.0	0.309	2.841	0.990	-	5.944	18.40	-	57.90	0.177	1192	2.057	-	0.325	[30]
Multan, Pakistan	6726	2.640	73.80	476.0	-	24.50	9242	-	9857	13.40	10,026	20.20	-	13.10	[34]
Uttar Pradesh, India	-	-	15.00	2652	42.90	-	-	-	-	-	-	38.30	105.3	159.9	[12]
Ranga Reddy district, India	-	-	27.00	67.80	29.20	-	-	-	-	-	-	28.30	202.0	77.10	[40]
Guwahati, India	-	18.00	122.9	124.4	124.4	-	-	-	-	194.8	-	170.5	-	286.0	[47]
Guanting Reservoir, China	-	0.390	-	16.78	2.860	-	-	-	-	-	-	1.740	-	23.00	[7]
Gorges areas, China	-	0.210	-	78.79	21.53	-	-	-	-	-	-	24.12	-	68.50	[35]
Yixing, China	5900	0.140	-	-	27.90	28,200	13,500	28.10	4400	303.9	10,400	43.40	-	66.90	[48]
Adana, Turkey	1.331	-	354.3	136.1	-	1.657	4.541	-	0.425	-	2.413	91.43	79.70	70.70	[19]
Murcia, SE Spain	-	0.230	-	19.18	11.84	-	-	-	-	149.7	-	67.91	-	21.57	[32]
Galicia, Spain	-	0.310	14.00	54.10	20.50	35,260	-	-	-	659.9	-	11.70	-	98.70	[5]
Ria de Vigo, Spain	-	0.30	-	-	31.10	-	-	-	-	-	-	55.62	-	114.05	[41]
Forest soils, France	-	0.222	3.87	34.64	10.56	-	-	-	-	-	-	38.38	-	46.50	[4]
Suszec Commune, Poland	-	0.80	-	34.43	8.47	-	-	-	-	-	-	39.80	-	62.47	[37]
Apulia, Italy	-	1.800	-	102.2	70.30	-	-	-	-	159.0	-	100.8	-	147.2	[49]
Veles, Macedonia	39,000	7.700	13.00	160	44.00	28,000	22,000	-	5100	840.0	10,000	220.0	210.0	280.0	[50]
Yocsina, Argentina	19,000	-	12.10	50.20	3.740	35,000	-	-	-	281.0	17,000	7.700	-	92.50	[51]
Central Victoria, Australia	-	-	9.76	13.25	13.95	29,462	-	-	-	213.3	-	16.58	-	273.2	[52]

a) Present study.

in the Table excluding Himalya, Pakistan [46] and Adana, Turkey [19]. The estimated levels of Pb in the present study were noticeably higher than those reported from Kasur and Mian Channun, Pakistan [30], Guanting reservoir, China [7], Galicia, Spain [5], Yocsina, Argentina [51] and Central Victoria, Australia [52]. The average levels of Sr were more or less comparable to the previously reported concentrations, however, mean level of Zn in the present study was comparatively lower than most of the reported levels and only comparable to those reported for Guanting reservoir, China [7], Murcia, Spain [32], and Forest soils, France [4].

In conclusion, the present study showed marked variations and diverse correlations of the selected metal contents in the water-extract and acid-extract of the soil samples during summer and winter. The distribution and covariation of selected metals in soils exhibited the seasonal variations, while, multivariate analysis revealed significant anthropogenic pollution of selected metals in the urban soils of Islamabad. Geoaccumulation index, enrichment factor and contamination factor exhibited moderate to high contamination of few metals in the soil samples during summer and winter. On the whole, considerable degree of contamination was observed in the soils; which was relatively higher in winter. Compared with the other studies around the world, generally the present metal levels were moderately less than most of the reported levels.

Acknowledgement

The research fellowship awarded by Quaid-i-Azam University, Islamabad, Pakistan to carry out this project is thankfully acknowledged.

References

- [1] A.K. Pendas, H. Pendas, Trace Elements in Soils and Plants, 3rd ed., CRS Press, Boca Raton, 2001.
- [2] D.C. Adriano, Trace Elements in Terrestrial Environments, Biogeochemistry, Bioavailability and Risks of Metals, Springer-Verlag, New York, 2001, p. 879.
- [3] O.A. Al-Khashman, R.A. Shawabkeh, Metals distribution in soils around the cement factory in southern Jordan, Environ. Pollut. 140 (2006) 387–394.
- [4] L. Hernandez, A. Probst, J.L. Probst, E. Ulrich, Heavy metal distribution in some French forest soils: evidence for atmospheric contamination, Sci. Total Environ. 312 (2003) 195–219.
- [5] A.F. Uria, C.L. Mateo, E. Roca, M.L.F. Marcos, Source identification of heavy metals in pasturelands by multivariate analysis in NW Spain, J. Hazard. Mater. 165 (2008) 1008–1015.
- [6] B.J. Alloway, D.C. Ayres, Chemical Principles of Environmental Pollution, 2nd ed., Blackie Academic and Professional, Chapman and Hall, London, 1997, pp. 208–211.
- [7] W. Luo, Y. Lu, J.P. Giesy, T. Wang, Y. Shi, G. Wang, Y. Xing, Effects of land use on concentrations of metals in surface soils and ecological risk around Guanting Reservoir, China, Environ. Geochem. Health 29 (2007) 459–471.
- [8] K.E. Giller, E. Witter, S.P. McGrath, Toxicity of heavy metals to microorganisms and microbial processes in agricultural soils: a review, Soil Biol. Biochem. 30 (1998) 1389–1414.
- [9] G.P. Cobb, K. Sands, M. Waters, B.G. Wixson, E. Doward-King, Accumulation of heavy metals by vegetables grown in mine wastes, Environ. Toxicol. Chem. 19 (2000) 600–607.
- [10] F.A. Nicholson, S.R. Smith, B.J. Alloway, C.C. Smith, B.J. Chambers, An inventory of heavy metals inputs to agricultural soils in England and Wales, Sci. Total Environ. 311 (2003) 205–219.
- [11] A.K. Pendas, A.B. Mukherjee, Trace Elements from Soil to Human, Springer-Verlag, Berlin, 2007.
- [12] S.S. Gowd, M.R. Reddy, P.K. Govil, Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the Ganga Plain, Uttar Pradesh, India, J. Hazard. Mater. 174 (2010) 113–121.
- [13] P.S. Hooda, R. Naidu, Speciation, bioavailability and toxicity relationships of contaminants in the terrestrial environment, in: Proceedings of International Contaminated Site Remediation Conference, Adelaide, South Australia, 15–18 September, 2004.
- [14] X. Wang, X. Shan, S. Zhang, B. Wen, A model for evaluation of the phytoavailability of trace elements to vegetables under the field conditions, Chemosphere 55 (2004) 811–822.
- [15] S.M. Rodrigues, B. Henriques, J. Coimbra, E.F. da Silva, M.E. Pereira, A.C. Duarte, Water-soluble fraction of mercury, arsenic and other potentially toxic elements in highly contaminated sediments and soils, Chemosphere 78 (2010) 1301–1312.

- [16] V. Ettler, M. Mihaljevic, O. Sebek, T. Grygar, Assessment of single extractions for the determination of mobile forms of metals in highly polluted soils and sediments – analytical and thermodynamic approaches, *Anal. Chim. Acta* 602 (2007) 131–140.
- [17] E. Pertsemli, D. Voutsas, Distribution of heavy metals in Lakes Doirani and Kerkini, Northern Greece, *J. Hazard. Mater.* 148 (2007) 529–537.
- [18] H.S. Ibrahim, M.A. Ibrahim, F.A. Samhan, Distribution and bacterial bioavailability of selected metals in sediments of Ismailia Canal, Egypt, *J. Hazard. Mater.* 168 (2009) 1012–1016.
- [19] M.G. Yalcin, A. Tumuklu, M. Sonmez, D.S. Erdag, Application of multivariate statistical approach to identify heavy metal sources in bottom soil of the Seyhan River (Adana), Turkey, *Environ. Monit. Assess.* 164 (2010) 311–322.
- [20] M. Ahmad, M.I.A. Khan, M. Nisar, M.Y. Kaleem, Study of pollution in Rawal Lake, *J. Chem. Soc. Pak.* 21 (1999) 47–49.
- [21] M.A. Rauf, M. Ikram, S. Shaukat, Water analysis of Rawal Lake and its surrounding areas, *J. Chem. Soc. Pak.* 24 (2002) 277–281.
- [22] M. Ashraf, M. Jaffar, J. Tariq, Copper, iron, lead and zinc concentration distribution and correlation in fish from fresh-water lakes, Pakistan, *Toxicol. Environ. Chem.* 42 (1994) 93–98.
- [23] S. Iram, I. Ahmad, K. Ahad, A. Muhammad, S. Anjum, Analysis of pesticides residues of Rawal and Simly lakes, *Pak. J. Bot.* 41 (2009) 1981–1987.
- [24] Pakistan Environmental Protection Agency, Report on Rawal Lake Catchment Area Monitoring Operation, Ministry of Environment, Islamabad, 2004.
- [25] M. Radojevic, V.N. Bashlin, *Practical Environmental Analysis*, The Royal Society of Chemistry, UK, 1999.
- [26] A. Yong, S.E. Hough, M.J. Abrams, H.M. Cox, C.J. Wills, G.W. Simila, Site characterization using integrated imaging analysis methods on satellite data of the Islamabad, Pakistan, region, *Bull. Seismol. Soc. Am.* 98 (2008) 2679–2693.
- [27] M.I. Sheikh, M.K. Pasha, V.S. Williams, S.Q. Raza, K.S.A. Khan, *Environmental geology of the Islamabad–Rawalpindi study area, northern Pakistan*, in: P.D. Warwick, B.R. Wardlaw (Eds.), *Regional Studies of the Potwar Plateau Area, Northern Pakistan*, U.S. Geological Survey, Reston, Virginia, 2007.
- [28] A. Fuentes, M. Llorens, J. Saez, M.S. Aguilar, A.B. Perez-Marín, J.F. Ortuno, V.F. Meseguer, Ecotoxicity, phytotoxicity and extractability of heavy metals from different stabilised sewage sludges, *Environ. Pollut.* 143 (2006) 355–360.
- [29] US-EPA, *Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils*, Method 3051A, Office of Solid Waste and Emergency Response, U.S. Government Printing Office, Washington, DC, 2007.
- [30] S.R. Tariq, M.H. Shah, N. Shaheen, Comparative statistical analysis of chrome and vegetable tanning effluents and their effects on related soil, *J. Hazard. Mater.* 169 (2009) 285–290.
- [31] StatSoft Inc., *STATISTICA for Windows*, Computer Programme Manual, Tulsa, OK, 1999.
- [32] J.A. Acosta, A. Faz, S.M. Martinez, Identification of heavy metal sources by multivariable analysis in a typical Mediterranean city (SE Spain), *Environ. Monit. Assess.* 169 (2010) 519–530.
- [33] S.R. Tariq, M.H. Shah, N. Shaheen, M. Jaffar, A. Khalique, Statistical source identification of metals in groundwater exposed to industrial contamination, *Environ. Monit. Assess.* 138 (2008) 159–165.
- [34] S.R. Tariq, N. Shaheen, A. Khalique, M.H. Shah, Distribution, correlation and source apportionment of selected metals in tannery effluents, related soils and groundwater – a case study from Multan, Pakistan, *Environ. Monit. Assess.* 166 (2010) 303–312.
- [35] W. Wu, D.T. Xie, H.B. Liu, Spatial variability of soil heavy metals in the three gorges area: multivariate and geostatistical analyses, *Environ. Monit. Assess.* 157 (2009) 63–71.
- [36] G. Muller, Index of geoaccumulation in sediments of the Rhine River, *J. Geol.* 2 (1969) 108–118.
- [37] K. Loska, D. Wiechula, I. Korus, Metal contamination of farming soils affected by industry, *Environ. Int.* 30 (2004) 159–165.
- [38] D.R. Lide, *CRC Handbook of Chemistry and Physics*, Geophysics, Astronomy, and Acoustics, Abundance of Elements in the Earth's Crust and in the Sea, 85th ed., CRC Press, Boca Raton, FL, 2005, Section 14.
- [39] C. Reimann, P. de Caritat, Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors, *Sci. Total Environ.* 337 (2005) 91–107.
- [40] S. Dantu, Heavy metals concentration in soils of southeastern part of Ranga Reddy district, Andhra Pradesh, India, *Environ. Monit. Assess.* 149 (2009) 213–222.
- [41] F.A. Vega, E.F. Covelo, B. Cerqueira, M.L. Andrade, Enrichment of marsh soils with heavy metals by effect of anthropic pollution, *J. Hazard. Mater.* 170 (2009) 1056–1063.
- [42] L. Hakanson, An ecological risk index for aquatic pollution control: a sedimentological approach, *Water Res.* 14 (1980) 975–1001.
- [43] G.C. Leong, *Monsoon Asia*, 4th ed., Oxford University Press, Singapore, 1992.
- [44] D.S. Manta, M. Angelone, A. Bellanca, R. Neri, M. Sprovieri, Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy, *Sci. Total Environ.* 300 (2002) 229–243.
- [45] R.A. Sutherland, Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii, *Environ. Geol.* 39 (2000) 611–627.
- [46] M.H. Shah, J. Iqbal, N. Shaheen, N. Khan, M.A. Choudhary, G. Akhter, Assessment of background levels of trace metals in water and soil from a remote region of Himalaya, *Environ. Monit. Assess.* (2011), doi:10.1007/s10661-011-2036-4.
- [47] M.J. Mahanta, K.G. Bhattacharyya, Total concentrations, fractionation and mobility of heavy metals in soils of urban area of Guwahati, India, *Environ. Monit. Assess.* 173 (2011) 221–240.
- [48] S. Wu, S. Zhou, X. Li, T. Jackson, Q. Zhu, An approach to partition the anthropogenic and natural components of heavy metal contaminations in roadside agricultural soil, *Environ. Monit. Assess.* 173 (2011) 871–881.
- [49] A. Buccolieri, G. Buccolieri, A. Dell'Atti, G. Strisciullo, R. Gagliano-Candela, Monitoring of total and bioavailable heavy metals concentration in agricultural soils, *Environ. Monit. Assess.* 168 (2010) 547–560.
- [50] T. Stafilov, R. Sajin, Z. Pancevski, B. Boev, M.V. Frontasyeva, L.P. Strelkova, Heavy metal contamination of topsoils around a lead and zinc smelter in the Republic of Macedonia, *J. Hazard. Mater.* 175 (2010) 896–914.
- [51] G.M.A. Bermudez, M. Moreno, R. Invernizzi, R. Pla, M.L. Pignata, Heavy metal pollution in topsoils near a cement plant: the role of organic matter and distance to the source to predict total and HCl-extracted heavy metal concentrations, *Chemosphere* 78 (2010) 375–381.
- [52] K. Sultan, Distribution of metals and arsenic in soils of Central Victoria (Creswick-Ballarot), Australia, *Arch. Environ. Contam. Toxicol.* 52 (2007) 339–346.