



## Short communication

## Time saving modified BCR sequential extraction procedure for the fraction of Cd, Cr, Cu, Ni, Pb and Zn in sediment samples of polluted lake

M.B. Arain<sup>a,1</sup>, T.G. Kazi<sup>a,\*</sup>, M.K. Jamali<sup>a,1</sup>, H.I. Afridi<sup>a,1</sup>, N. Jalbani<sup>b,2</sup>, R.A. Sarfraz<sup>a,1</sup>, J.A. Baig<sup>a,1</sup>, G.A. Kandhro<sup>a,1</sup>, M.A. Memon<sup>c,3</sup><sup>a</sup> Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan<sup>b</sup> Pakistan Council for Scientific and Industrial Research, University Road, Karachi 75280, Pakistan<sup>c</sup> Institute of Chemistry, University of Sindh, Jamshoro 76080, Pakistan

## ARTICLE INFO

## Article history:

Received 17 November 2007

Received in revised form 23 February 2008

Accepted 25 February 2008

Available online 4 March 2008

## Keywords:

Polluted lake

Sediment

Metal distribution

Sequential extraction

## ABSTRACT

The mobility, availability and persistence of heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) in contaminated lake sediment samples were evaluated by means of sequential extraction scheme, proposed by the Community Bureau of Reference protocol (BCR). The metal content in the extracts was measured by atomic absorption spectrometry. The precision and accuracy of the proposed procedure were evaluated by using a certified reference material BCR 701. The maximum recoveries for heavy metals (HMs) were observed for all three steps of BCR protocol at 32 h total shaking period instead of previously reported 51 h, with  $p > 0.05$ . The lixiviation tests (DIN 38414-S4) were used to evaluate the leaching of HMs from sediment samples and it was observed that levels of water extractable HMs were low as compared to those values obtained by acid-soluble fraction of the BCR protocol.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Heavy metals (HMs) are considered as serious inorganic pollutants because of their toxic effects on life in aquatic system, having a high enrichment factor and slow removal rate [1]. Sediments function as a sink for HMs from diverse sources, reflecting the natural soil composition of the surrounding areas, as well as human activities. In an aquatic environment, HMs are subjected to precipitation, complexation, adsorption and solubilization reactions, depending on the physical and chemical characteristics of the water body [2]. The lake sediments conserve valuable historic information on past and present conditions of lakes and their environments for HMs [3].

Measurements of total metal content are a poor indicator of metal bioavailability, mobility or toxicity, when these properties basically depend on the chemical association of the different components of the sample [4]. Single and sequential extraction

methods have been widely applied to characterise the chemical forms in which trace metals are present in soils, sediments and sludges [5,6]. In 1987, the European Standards, Measurement and Testing (SM&T) Programme, formerly Community Bureau of Reference (BCR), launched a project to harmonise measurements of the extractable trace-metal content in soils and sediments, which is a good compromise method that gives information on the environmental contamination risk [7]. According to Quevauviller [8], the determination of specific chemical forms, or the nature of binding, is much more valuable than the determination of the total metal content, since the toxic effects and the geochemical pathways of elements are determined mainly by their mobile species.

In BCR sequential extraction schemes, extractants are applied in order of increasing reactivity so that the successive fractions obtained correspond to metal association forms with lesser mobility. The extractants commonly used in BCR sequential extraction schemes fall generally within the following groups: acetic acid 0.11 M (step 1); reducing agents (step 2); oxidizing agents (step 3) [9]. Traces of HMs speciation studies are important because slight changes in metal availability and in environmental conditions can cause these elements to be toxic to animals and plants. In order to study metal speciation in sediments, leaching/extraction tests are widely used for the assessment of elements mobilization [10].

The aim of this work was to improve the modified BCR procedure [11], by reducing the shaking time on mechanical shaker for

\* Corresponding author. Tel.: +92 22 2771379; fax: +92 22 2771560.

E-mail addresses: [tgkazi@yahoo.com](mailto:tgkazi@yahoo.com) (T.G. Kazi), [bilal.ku2004@yahoo.com](mailto:bilal.ku2004@yahoo.com) (M.B. Arain), [mkhanjamali@yahoo.com](mailto:mkhanjamali@yahoo.com) (M.K. Jamali), [hassanimranafriidi@yahoo.com](mailto:hassanimranafriidi@yahoo.com) (H.I. Afridi), [nusratjalbani.21@yahoo.com](mailto:nusratjalbani.21@yahoo.com) (N. Jalbani), [rajaadilsarfraz@gmail.com](mailto:rajaadilsarfraz@gmail.com) (R.A. Sarfraz), [jab.ughal@yahoo.com](mailto:jab.ughal@yahoo.com) (J.A. Baig), [gakandhro@yahoo.com](mailto:gakandhro@yahoo.com) (G.A. Kandhro), [mamemon21@yahoo.com](mailto:mamemon21@yahoo.com) (M.A. Memon).

<sup>1</sup> Tel.: +92 22 2771379; fax: +92 22 2771560.<sup>2</sup> Tel.: +92 218142895 8; fax: +92 218141847.<sup>3</sup> Tel.: +92 22 2772704; fax: +92 22 2771681.

each step, applied to leaching of heavy metals from lake sediment. Analytical methodology assessment has been carried out using a reference material BCR 701. The sample mass from 0.1 g to 1.0 g and different time intervals (6–16 h) for shaking were also investigated. Furthermore, in order to gain additional information about more easily mobilized metal forms in the lake sediment; a leaching test, which is based on a German Standard Method, was used [12]. The total burdens of Cd, Cr, Cu, Ni, Pd, and Zn in sediment samples were determined after microwave-assisted acid digestion with aqua-regia. Analyses of the extracts and digests were performed by flame atomic absorption spectrometry/electrothermal atomic absorption spectrometry (FAAS/ETAAS).

## 2. Experimental

### 2.1. Sampling sites and sample collection

Manchar is the biggest shallow water natural lake of Pakistan, situated at a distance of about 18 km (26°3'N:67°6'E) from Sehwan Sharif, District Jamshoro, Sindh. It is a vast natural depression flanked by the Khirthar hills in the west, the Laki hills in the south and the river Indus in the east. The mean depth of Manchar lake is approximately 2.5–3.75 m and covering area is 233 km<sup>2</sup>. The human activities have been changing significantly the original regime of the lake over the last 50 years. Sediment samples were collected from the top 10-cm layer to the bottom at Manchar lake in 2005–2006 on monthly basis. A hole dug with a motor-driven excavator was used to collect the sediments. From each station five samples of sediment soil were collected randomly in clean polypropylene bags. The temperature was recorded on the sampling site. In the laboratory, all of the sediments were mixed together and made representative sample and spread on plastic trays in fume cupboards and allowed to dry at an ambient temperature. After air drying for 8 days, the representative samples were ground in a centrifugal ball mill in order to homogenize them and passed through a 500- $\mu$ m nylon fiber sieve and were kept in polypropylene containers at an ambient temperature before analysis.

### 2.2. Chemicals and reagents

Ultrapure water obtained from ELGA Labwater System (Bucks, UK) was used throughout the work. The extractant solutions as listed in Fig. 1, and all other solutions were prepared from analytical grade reagents (Merck, Darmstadt, Germany) and were checked for possible trace-metal contamination. Standard solutions of Cd, Cr, Cu, Pb, Ni and Zn were prepared by dilution of certified standard solutions (1000 mg/L) Fluka Kamika (GmbH CH-9471, Buchs, Switzerland). 99.99% pure argon, used as sheath gas for the atomizer and for internal purge. Due to unavailable certified samples of sediment, we check the reproducibility of methods by BCR 701 sediment sample (Certified Reference Material, European Commission, Brussels). All glassware and plastic material used were previously treated for 1 week in 2M supra pure nitric acid and rinsed with distilled water and then with ultrapure water. Recommended modifiers, magnesium nitrate and palladium (0.001 mg Pd + 0.0015 mg Mg(NO<sub>3</sub>)<sub>2</sub>) for Cd; ammonium phosphate (0.2 mg NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>) for Pb; magnesium nitrate (0.05 mg Mg(NO<sub>3</sub>)<sub>2</sub>) for Cr and Ni were prepared from NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, Mg(NO<sub>3</sub>)<sub>2</sub> (Merck), Pd 99.999% (Sigma).

### 2.3. Apparatus

A WTW 740 pH meter was employed for pH adjustments of the solutions. A conductivity meter (WTW Cond. 720 Germany), a WIROWKA Laboratoryjna type WE-1, nr-6933 centrifuge machine

(speed range 0–6000 rpm, timer 0–60 min, 220/50 Hz, Mechanika Pheczyjina, Poland) and a PM023 domestic programmable PEL microwave oven (PEL Japan) were used. A horizontal flask electrical shaker (220/60 Hz, Gallenkamp, England) was used for shaking the samples. HMs were determined in digests and extracts by an atomic absorption spectrometer (Hitachi Ltd., Model 180–50, S.N. 5721–2) equipped with a 10-cm burner head and graphite furnace G–03. Hollow-cathode lamps of each metal were used as a radiation source. Resonance lines at 228.8, 357.9, 324.8, 232.0, 283.3 nm and 213.8 nm were used for Cd, Cr, Cu, Ni, Pb and Zn, respectively. Electrothermal atomization programme and modifiers were used as reported elsewhere [13]. The contents of Cu and Zn were measured by FAAS, while Cd, Cr, Pb and Ni were determined by ETAAS.

### 2.4. Physico-chemical studies

The physico-chemical parameters (i.e. pH, organic matter, organic carbon, total nitrogen, sulphur, phosphate and silica) of 24 batches of sediment samples (triplicate of each batch) were performed by standard methods. The pH values were determined of each batch, using a ratio of 1:2.5 (sediment and ultrapure water). The organic carbon was determined by Walkley–Black method [14]. Organic matter content was obtained by ashing duplicate samples of each batch of sediment in muffle furnace at 540 °C for 6 h. The difference between the dry weight of sediment samples before and after ashing was used for the calculation of organic matter content. Total sulphate-sulphur was determined by turbidity method [15]. PO<sub>4</sub>-P was measured by molybdate–ascorbic acid method, total nitrogen was determined by Kjeldahl's method [16,17]. After digestion with nitric acid, the digestion solution was filtered through a Whatman 42 filter paper into a volumetric flask. After drying at 105 °C, the residue on the filter paper was weighed and calculated as silica [18].

### 2.5. BCR three-step sequential extraction procedure

The BCR three-step sequential extraction procedure was modified as shown in Fig. 1 [11]. In order to determine the optimum amount of samples to be analyzed, model experiments were performed with various amounts of the samples. After the optimization we used 0.5 g sediment samples, and for practical reasons, the weight of sample and volume of extractant were reduced by half, so that the weight-to-volume ratio was the same as in the original BCR extraction scheme. The extractant reagents were added subsequently for 1–3 steps, and shaken in end-over-end mechanical shaker for different time intervals (4–16 h at room temperature 25–35 °C), it was observed that optimum recovery of HMs required 8–10 h, compared to that encountered in most other researches (working at 20 °C) [19,20], due to the warm climate of our country. So for the rest of all the experiment, 10 h duration for mechanical shaking was applied. The detail of the experiments by using BCR sequential extraction protocol was reported in our previous work [21], and a brief summary of BCR sequential extraction is shown in Fig. 1.

### 2.6. Leaching test (DIN 38414-S4)

This leaching test provides information about the behavior of a sediment sample when it comes in contact with water. Details of the experimental protocol were followed from the German Standard Method [12]. In this leaching test ultrapure water is used as an extractant. 5.0 g of air-dried duplicate samples of sediment of each batch were weighed into Pyrex flasks. Leaching was then performed at room temperature for a period of 12–24 h using a ratio of 1:10 (sediment:ultrapure water). After

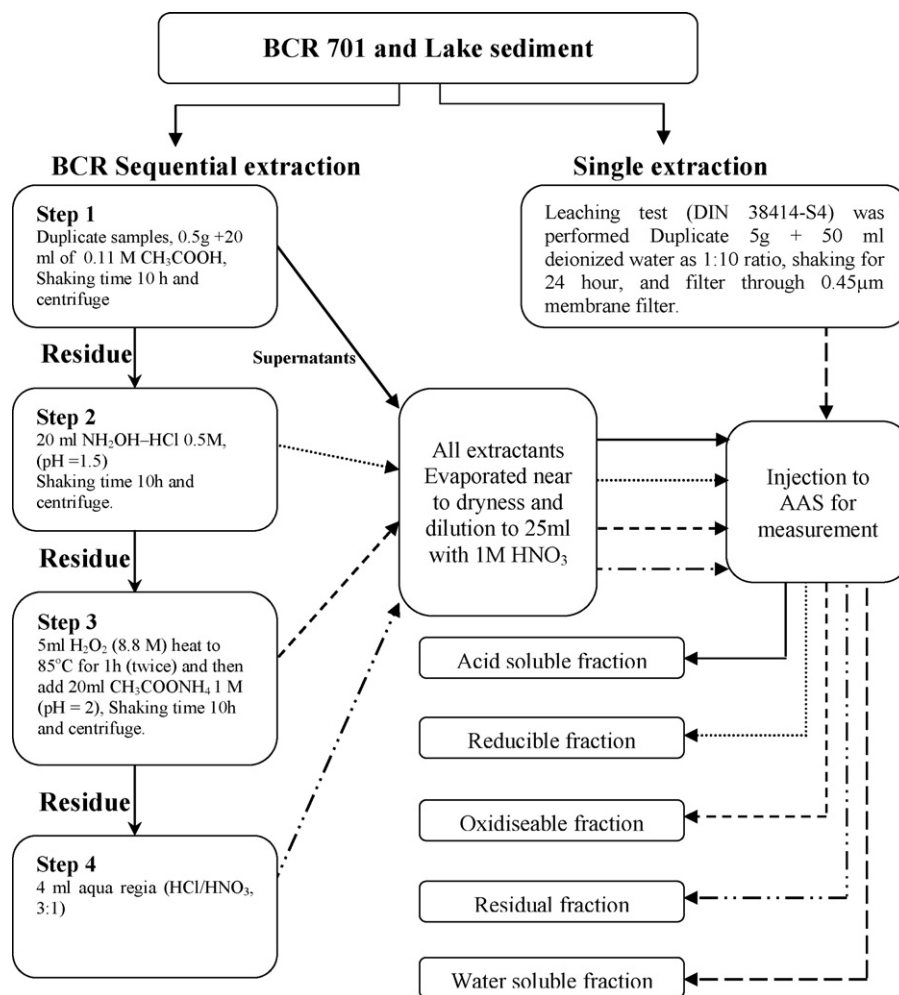


Fig. 1. Flow diagram of the modified BCR sequential and DIN 38414-S4 single extraction procedures.

different leaching periods, the undissolved residue was separated by filtration using a membrane filter of pore size  $0.45\ \mu\text{m}$  pre-washed with ultrapure water. Finally, the pH values, electrical conductivity and concentration of the analytes were measured. The maximum recoveries of toxic metals were obtained after 24 h.

### 2.7. Evaluation of analytical performance

The analytical performance of this laboratory procedure was evaluated by analyzing certified reference material CRM 701. We analyzed six replicate samples for each step, and reported the obtained values (mg/kg) on dried mass basis, and compared with certified values of all understudy HMs [8]. Uncertainty is expressed as S.D. The comparison between time saving sequential extraction methods and modified BCR sequential extraction (SEB) was calculated by paired  $t$ -test, and compared the  $t_{\text{Experimental}}$  ( $t_{\text{Exp.}}$ ) to that of theoretical value at a 5 d.f. ( $\alpha=0.05$ ). In all cases the  $t_{\text{Exp.}}$  is less than that of the theoretical value, i.e. no differences between the extractable HMs by proposed time saving extractions and SEB. In all cases, metal recovery was calculated as the following ratio:

$$\text{Recovery (\%)} = \frac{\text{HMs extracted by time saving sequential extraction}}{\text{HMs extracted by SEB}} \times 100$$

## 3. Results and discussion

### 3.1. Sediment characteristics

The pH values of 24 batches of sediment samples collected from five locations of Manchar lake were observed to be in the range of 7.81–8.05. The considerable amount of sulphate-sulphur and phosphate were found in the range of 932–1294 mg/kg and 453–510 mg/kg, respectively, which indicate the addition of runoff agricultural wastes in lake [22]. The organic matter is a component of great importance although the level in sediment samples is low (18.0–22.1%) because it tends to form soluble or insoluble complexes with elements, to migrate or to be retained in the sediment. The organic carbon, silica content and total nitrogen in all sediment samples were 10.4–12.9%, 79.1–80.5% and 1436–2010 mg/kg, respectively.

### 3.2. Sequential extraction of HMs in lake sediment

The sediment existing at the bottom of the water column plays a major role in the pollution scheme of the lake system by elements. They reflect the current quality of the water system and can be used to detect the presence of contamination that does not remain soluble after discharging into water. Each metal in air-dried sediment samples has its own pattern regarding the distribution over the four fractions (acid soluble, reducible, oxidisable and residual). Precision and accuracy of proposed BCR sequential

**Table 1**  
Time-saving BCR sequential extractable metal contents in BCR 701 ( $n=6$ ), based on the mean  $\pm$  S.D. (mg/kg dried basis)

Metals		Cd	Cr	Cu	Ni	Pb	Zn
First step	Certified values [8]	7.34 $\pm$ 0.35	2.26 $\pm$ 0.16	49.3 $\pm$ 1.7	15.4 $\pm$ 0.9	3.18 $\pm$ 0.21	205 $\pm$ 6.0
	This work	7.30 $\pm$ 0.40	2.32 $\pm$ 0.20	49.0 $\pm$ 1.4	15.9 $\pm$ 1.2	3.17 $\pm$ 0.32	204 $\pm$ 10.5
	Recovery (%) ( $t_{Exp.}$ )	99.4(0.8)	102(0.1)	99.4 (0.7)	103(0.3)	99.7 (0.1)	99.6 (0.9)
Second step	Certified values	3.77 $\pm$ 0.28	45.7 $\pm$ 2.0	124.0 $\pm$ 3.0	26.60 $\pm$ 1.28	126.00 $\pm$ 3.0	114.0 $\pm$ 5.0
	This work	3.80 $\pm$ 0.25	45.3 $\pm$ 1.7	123.8 $\pm$ 2.6	26.2 $\pm$ 1.6	125.9 $\pm$ 2.5	113.8 $\pm$ 6.9
	Recovery (%) ( $t_{Exp.}$ )	100(0.6)	99.1 (0.5)	99.8 (0.8)	98.5 (0.2)	99.9 (0.3)	99.8 (0.4)
Third step	Certified values	0.27 $\pm$ 0.006	143.0 $\pm$ 7.0	55.2 $\pm$ 4	15.3 $\pm$ 0.9	9.28 $\pm$ 2.0	45.7 $\pm$ 4.0
	This work	0.27 $\pm$ 0.02	143.2 $\pm$ 6.3	55.6 $\pm$ 3.4	15.5 $\pm$ 0.7	9.25 $\pm$ 0.76	45.3 $\pm$ 4.2
	Recovery (%) ( $t_{Exp.}$ )	98.9 (0.9)	100(0.7)	100(0.9)	101 (0.1)	99.7 (0.1)	99.1 (0.7)
	Residual (SEB)	0.23 $\pm$ 0.02	66.7 $\pm$ 4.3	40.5 $\pm$ 2.7	41.3 $\pm$ 2.2	11.4 $\pm$ 1.0	95.4 $\pm$ 7.8
	$\sum$ three steps + residual (SEB)	11.6 $\pm$ 0.5	257.5 $\pm$ 10.1	269 $\pm$ 9	98.9 $\pm$ 3.1	149.7 $\pm$ 9.6	458.7 $\pm$ 15.3
	Pseudo-total	11.6 $\pm$ 0.7	258.0 $\pm$ 9.4	268.3 $\pm$ 8.8	99.2 $\pm$ 4.9	148.6 $\pm$ 5.9	457.9 $\pm$ 17.5
Relative error (%) <sup>a</sup>	0.09	-0.19	0.22	-0.30	0.75	0.17	

<sup>a</sup> Relative error (%) =  $\{[(\text{sum of three steps} + \text{residual}) - \text{pseudo-total}] / \text{pseudo-total}\} \times 100$ ,  $t_{critical} = 2.570$  (d.f. = 5).

**Table 2**  
Elemental partitioning in lake sediment samples by time saving optimized BCR method ( $n=72$ )

Heavy metals	Cd	Cr	Cu	Ni	Pb	Zn
First step	1.82 $\pm$ 0.19	0.52 $\pm$ 0.04	3.32 $\pm$ 0.28	2.66 $\pm$ 0.2	0.46 $\pm$ 0.04	34.8 $\pm$ 2.8
Second step	2.36 $\pm$ 0.19	8.78 $\pm$ 0.66	9.82 $\pm$ 0.68	8.66 $\pm$ 0.8	10.0 $\pm$ 1.0	33.5 $\pm$ 2.8
Third step	2.28 $\pm$ 0.2	7.18 $\pm$ 0.52	4.34 $\pm$ 0.22	3.72 $\pm$ 0.3	1.92 $\pm$ 0.17	17.0 $\pm$ 1.0
Residual (R)	0.76 $\pm$ 0.06	4.70 $\pm$ 0.04	3.54 $\pm$ 0.24	6.40 $\pm$ 0.5	7.46 $\pm$ 0.6	16.6 $\pm$ 1.4
$\sum$ three step + R	7.22 $\pm$ 0.34	21.2 $\pm$ 0.7	21.0 $\pm$ 0.8	21.4 $\pm$ 0.4	19.8 $\pm$ 1.2	102 $\pm$ 4
Pseudo-total	7.16 $\pm$ 0.50	21.2 $\pm$ 2.1	20.9 $\pm$ 1.8	21.4 $\pm$ 2.1	19.8 $\pm$ 2.0	100 $\pm$ 7
Relative error (%)	+0.84	-0.09	+0.19	-0.09	+0.20	+1.84

All values reported as mean  $\pm$  S.D. (mg/kg dried basis)

extraction were assessed using six replicates from a single bottle of BCR 701 (Table 1). The results showed a good agreement between the obtained and the certified values for the metals analyzed [8]. As can be seen, no significant differences were observed between the pseudo-total metal content, following the aqua-regia digestion and the sum of extracted metals following the sequential extraction procedure. Low relative errors (0.75%) indicate the good quality results.

The fractionations of HMs under study in lake sediments are shown in Table 2. The results predicted that all HMs are mainly associated with reactive forms (released in the first three steps of the sequential extraction procedure). Among the metals studied the Cd and Zn were extracted predominantly in the first step of the sequential extraction (1.6–2.1 mg/kg and 29.4–25.6 mg/kg), respectively, which represents the metal bound to carbonates or sorbed/exchangeable phases [23]. On the other hand, only very small fractions of Pb and Cr (0.20–0.70 mg/kg and 0.40–0.58 mg/kg, respectively) were present as acid exchangeable species in all sediment samples collected from five stations of the lake. The proportion of the metals in the acid-soluble fraction followed the order Zn > Cd > Cu > Ni > Pb > Cr (Table 2).

The major associations of all elements in lake sediment samples were extracted from reducible phase, that account for the range of 3.3–5.1 mg/kg, 1.7–3.1 mg/kg, 7.9–9.7 mg/kg, 7.1–11.6 mg/kg, 7.0–12.4 mg/kg, 8.0–11.2 mg/kg and 29.6–36.2 mg/kg for Cd, Cr, Cu, Ni, Pb and Zn, respectively, and average result was shown in Table 2. The surfaces of Fe and Mn oxides have special affinity with the cations to natural pH. This is consistent with results obtained by several authors, who found that Fe and Mn hydroxides are important scavengers of these elements in sediments [24].

The range of extractable Cd in oxidisable fractions was observed as 2.0–2.8 mg/kg in different catchment stations, shows the increase incoming of these toxic elements in the lake, probably due to the input of organic matter from domestic sewage and other human activities, from the villages located close to the banks

of Manchar Lake. The major portion of Pb was associated with the residual phase, which accounted for about 30.7–47.2% of the total contents of Pb.

### 3.3. Leaching test with DIN 38414-S4 standard procedure

The leaching test was applied in order to assess the behavior of Cd, Cr, Cu, Ni, Pb and Zn in terms of mobility and environmental concern. The potential leachability of elements without external pH influence may occur as a result of different sample pH values. Comparison of acid-soluble fraction of three-stage sequential extraction scheme and leaching test was also applied in order to assess the behavior of elements in terms of mobility and environmental concern. The water-soluble fraction has metals in the range of 0.23–0.32 mg/kg, 0.07–0.12 mg/kg, 0.32–0.46 mg/kg, 0.068–0.34 mg/kg and 0.91–2.62 mg/kg for Cd, Cr, Cu, Ni, Pb and Zn, respectively, average results were shown in Table 3. The acid-soluble fraction (CH<sub>3</sub>COOH 0.11 M) may indicate which metals are more mobile and therefore most available for biota of aquatic system of lake. On the other hand, the use of leaching tests such as DIN 38414-S4 enables one to evaluate the potential environmental risks associated with pollutants lixiviation under water. The concentrations of all HMs analyzed in water leachate were comparatively

**Table 3**  
Heavy metals leachability by water (DIN 38414-S4) and contamination factors ( $C_f$ ) of lake sediment samples ( $n=72$ )

Parameters	mean $\pm$ S.D. (mg/kg)	$C_f$
pH	7.81 $\pm$ 0.05	
Conductance ( $\mu\text{S}/\text{cm}$ )	1166 $\pm$ 208	
Cd	0.38 $\pm$ 0.01	8.5
Cu	0.30 $\pm$ 0.06	4.9
Cr	0.12 $\pm$ 0.02	3.5
Ni	0.45 $\pm$ 0.03	2.3
Pb	0.34 $\pm$ 0.01	1.6
Zn	1.17 $\pm$ 0.09	5.13

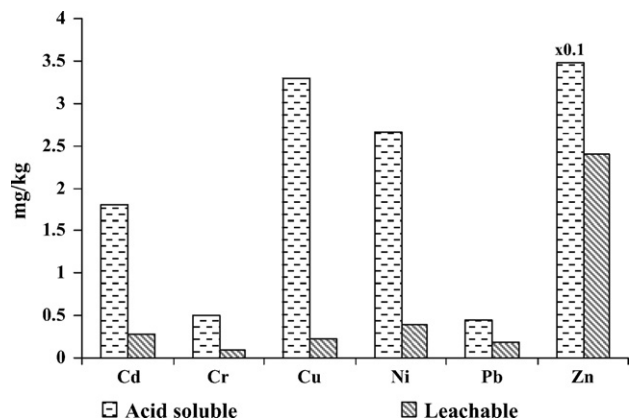


Fig. 2. Comparison of exchangeable heavy metals obtained in step one of the BCR scheme and DIN 38414-S4 leaching.

lower than acid-soluble fraction of all metals (Fig. 2). Therefore it can be concluded that leachability by pure water was strongly depend on the sediment pH.

#### 3.4. Environmental implications

To study HMs retention in sediment samples, the individual contamination factors ( $C_f$ ) of elements in sediment samples collected from five stations were calculated. In this work,  $C_f$  was calculated as the sum of concentrations of metals extracted in the first three steps of the sequential extraction divided by the concentration in the residual fraction (extracted with concentrated aqua-regia from the residue of the sequential extraction) [25].

The experimental results indicated that among the HMs, Cd and Zn gave the highest  $C_f$  values, 6.0–9.6 and 3.4–9.2, respectively, in all sediment samples collected from different spots of Manchar lake, followed by Cu and Cr having comparatively lower  $C_f$  values, 3.7–6.0 and 3.3–3.9, respectively, they have strong association with reducible fraction (Table 3). In general way Ni and Pb well retained in the sediment samples, and gave lower  $C_f$  values. Owing to the high toxicity of Cd, the  $C_f$  values obtained represent a potential risk of contamination to the water phase, or to the biota, in the samples from all stations.

#### 4. Conclusion

The applications of sequential extraction methods to environmental samples provide relevant information about possible toxicity when they are discharged into the environment. In this study the minimized time interval for optimized BCR three-step extraction procedure, that was validated by using a certified reference material, BCR 701, and the proposed approach allowed us to obtain similar results in 32 h, to the conventional procedure obtained after 51 h. Cd and Zn occurred more abundantly in soluble form than did other elements. Comparison among the more mobile element fraction obtained from step 1 of the BCR scheme and DIN 38414-S4 shows that the results of HMs obtained by lixiviation in water are low. Agricultural, industrial effluents and domestic wastes discharged directly into the lake are responsible for the HMs pollution.

#### References

- [1] J. Alloway, D.C. Ayres, Chemical Principles of Environmental Pollution, Chapman & Hall, UK, 1997.
- [2] Y.J. An, D.H. Kampbell, Total, dissolved, and bioavailable metals at Lake Texoma marinas, Environ. Pollut. 122 (2003) 253–259.
- [3] H. Ozmen, F. Kulahci, A. Cukurovali, M. Dogru, Concentrations of heavy metal and radioactivity in surface water and sediment of Hazar Lake: Elazig, Turkey, Chemosphere 55 (2004) 401–408.
- [4] M. Tuzen, H. Sari, M. Soylak, Microwave and wet digestion procedures for atomic absorption spectrometric determination of trace metals contents of sediment samples, Anal. Lett. 37 (2004) 1925–1936.
- [5] E.D. Hullebusch, S. Utomo, M.H. Zandvoort, P.N.L. Lens, Comparison of three sequential extraction procedures to describe metal fractionation in anaerobic granular sludges, Talanta 65 (2005) 549–558.
- [6] A. Fuentes, M. Liorens, J. Saez, M.I. Aguilar, J.F. Ortuno, V.F. Meseguer, Comparative study of six different sludges by sequential speciation of heavy metals, Biores. Technol. 99 (2008) 517–525.
- [7] Ph. Quevauviller, G. Rauret, H. Muntau, A.M. Ure, R. Rubio, J.F. Lopez-Sanchez, H.D. Fiedler, B. Griepink, Evaluation of a sequential extraction procedure for the determination of extractable trace metal contents in sediments, Fresen. J. Anal. Chem. 349 (1994) 808–814.
- [8] Ph. Quevauviller, Operationally defined extraction procedures for soil and sediment analysis. I. Standardization, Trac-Trend. Anal. Chem. 17 (1998) 289–298.
- [9] C. Gleyzes, S. Tellier, M. Astruc, Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures, Trac-Trend. Anal. Chem. 21 (2002) 451–467.
- [10] A.M. Ure, Ph. Quevauviller, H. Muntau, B. Griepink, Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the Auspices of the BCR of the Commission of the European Communities, Int. J. Environ. Anal. Chem. 51 (1993) 135–151.
- [11] G. Rauret, J.F. Lopez-Sanchez, A. Sahuquillo, R. Rubio, C.M. Davidson, A.M. Ure, Ph. Quevauviller, Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials, J. Environ. Monit. 1 (1999) 57–61.
- [12] DIN 38414-S4, German standards methods for the examination of water, waste water, sludge; group S (sludge, sediments), determination of leachability by water (S4), 1984.
- [13] M.B. Arain, T.G. Kazi, M.K. Jamali, N. Jalbani, H.I. Afridi, A. Shah, Total dissolved and bioavailable elements in water and sediment samples and their accumulation in *Oreochromis mossambicus* of polluted Manchar Lake, Chemosphere 70 (2008) 1845–1856.
- [14] J.M. Bartels, in: D.L. Sparks (Ed.), Methods of Soil Analysis. Part III. Chemical Methods, Soil Science Society of America, Madison, Wisconsin, USA, 1996, pp. 1201–1230.
- [15] T.G. Kazi, S.A. Katz, Determination and estimation of different forms of sulphur in soil and sewage sludge, J. Anal. Environ. Chem. 1 (1990) 67–73.
- [16] L.S. Clesceri, A.E. Greenberg, A.D. Eaton (Eds.), Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), Washington, DC, 1998.
- [17] Association of Official Analytical Chemists, AOAC, Official Methods of Analysis, 16th ed., AOAC International, Gaithersburg, MD, 1995.
- [18] V. Reeuwijk, L.P. Editor, Procedures for Soil Analysis, 3rd ed., International Soil Reference and Information Centre, Wageningen, The Netherlands, 1992.
- [19] C.M. Davidson, A.M. Ure, Ph. Quevauviller, Some sources of variability in application of the three-stage sequential extraction procedure recommended by BCR to industrially contaminated soil, Fresen. J. Anal. Chem. 363 (1999) 446–451.
- [20] M. Soylak, U. Uzek, I. Narin, M. Tuzen, O. Turkoglu, L. Elci, Application of the sequential extraction procedure for dust samples from Kayseri-Turkey, Fresen. Environ. Bull. 13 (2004) 454–457.
- [21] T.G. Kazi, M.K. Jamali, G.H. Kazi, M.B. Arain, H.I. Afridi, A. Siddiqui, Wastewater sludge using a BCR sequential extraction procedure and a leaching test, Anal. Bioanal. Chem. 383 (2005) 297–304.
- [22] T.A. Khan, Limnology of four saline lakes in western Victoria, Australia, Limnologia 33 (2003) 316–326.
- [23] E.K.A. Hudson, M.G. Macklin, C.D. Curtis, D. Vaughan, Processes of formation and distribution of Pb-, Zn-, Cd-, and Cu-bearing minerals in the Tyne Basin, Northeast England: implications for metal-contaminated river systems, Environ. Sci. Technol. 30 (1996) 72–80.
- [24] E.J. Dawson, M.G. Macklin, Speciation of heavy metals in floodplain and flood sediments: a reconnaissance survey of the Aire Valley, West Yorkshire, Great Britain, Environ. Geochem. Health 20 (1998) 67–76.
- [25] M.K. Jamali, T.G. Kazi, H.I. Afridi, M.B. Arain, N. Jalbani, A.R. Memon, Speciation of heavy metals in untreated domestic wastewater sludge by time saving BCR sequential extraction method, J. Environ. Sci. Health A 42 (2007) 649–659.