Mine Water Environ (2012) 31:29–39
DOI 10.1007/s10230-012-0171-y

TECHNICAL ARTICLE

Trace Metal Occurrence and Mobility Assessment in Stream Sediments near the Sungun Porphyry Copper Deposit in Northwest Iran

F. Moore · A. A. Aghazadeh

Received: 6 June 2011 / Accepted: 26 January 2012 / Published online: 22 February 2012

Abstract The Sungun porphyry copper deposit is located 100 km northeast of Tabriz in the Azarbaijan province of Iran. The total concentration and chemical fractionation of metals and metalloids (As, Se, Cd, Cr, Ni, Co, and Zn) in sediment downstream of the Sungun mine was investigated. The degree of contamination was evaluated using the sediment pollution index (SPI) and enrichment factor. The concentrations of As, Cd, Se, and Zn in the contaminated sediments were elevated due to anthropogenic activities. According to the SPI, surface sediments in the ephemeral rivers flowing in the vicinity of the Sungun porphyry copper deposit are classified as natural sediment with no ecological risk, while sediments that received contaminated effluents are classified as slightly polluted. Sequential extraction indicated that Co was principally associated with the iron and manganese oxide fraction, while other elements (As, Zn, Cr, Se, and Ni) were mainly distributed in residual phases. Cadmium is the only element that has a high potential for mobility and bioavailability in the sediments and, of the investigated elements, it poses the greatest potential risk to the local aquatic ecosystems. The chemical fractionation pattern of elements appears to be influenced by industrial effluents. Although the bioavailable fraction of most contaminant metals is low due to the freshness of the sediments, over time, the oxidation of sulfide minerals in these sediments could contribute contaminant elements in soluble form.

Keywords Contaminant metals · Enrichment factor · Mobility factor · Sediment · Sequential extraction

F. Moore · A. A. Aghazadeh (✉)
Department of Earth Sciences, College of Sciences,
Shiraz University, Shiraz, Iran
e-mail: azizeh_aghazadeh@yahoo.com

Introduction

Weathering of soils and rocks, atmospheric deposition, and mining are important sources of trace metals in sediments (Cevik et al. 2009). Although mining affects a relatively small area, it can have a significant environmental impact, depending on factors such as climate, mining methods, geological conditions, and whether the mine is active or abandoned (Bell et al. 2001). River sediments act as a sink and source for a variety of environmental contaminants and provide a record of stream pollution inputs into aquatic ecosystems (Cevik et al. 2009; Milenkovic et al. 2005). Changes in environmental conditions, such as acidification, redox potential, organic ligand concentrations, or salinity, can mobilize trace elements and contaminate surrounding waters (Gonzaleza et al. 2000; Milenkovic et al. 2005; Yuan et al. 2004).

Sequential extraction has been widely applied to evaluate the potential mobility of trace elements and how trace elements are linked to soil and sediment phases (Guo et al. 2007; Shiowatana et al. 2001; Zemberyová et al. 2006). It can provide information about the origin, chemical form, source of trace metals (Shiowatana et al. 2001; Tessier et al. 1979; Zemberyová et al. 2006) and has been used to study the bioavailability and fate of metals and metalloids in the environment (Shiowatana et al. 2001). Sequential extraction generally follows the sequence: unbuffered salts, weak acids, reducing agents, oxidizing agents, and strong acids (Guo et al. 2007). Major potential problems in sequential extraction procedures are the non-selectivity of extractants and trace metal readsorption during phase extractions (Guo et al. 2007). The most commonly employed sequential extraction procedures are those developed by Tessier et al. (1979), and the Commission of the European Communities Bureau of Reference (BCR)

Standards Measurement and Testing Program; Guo et al. (2007); Quevauviller (1998). The BCR method is a three-step sequential extraction procedure, which has been applied to a variety of matrices, including sediments (Zemberyová et al. 2006). This extraction method harmonizes different extraction procedures for sediment analysis and allows comparison between results obtained in different laboratories (Ure et al. 1993). In this study, we used sequential extraction to characterize total content and BCR chemical fractionation pattern of As, Cd, Zn, Cr, Co, Se, and Ni in sediments in the vicinity of the Sungun porphyry copper mine to obtain information about their bioavailability and whether they posed a potential risk to the environment.

Geology and Site Characteristics

The Sungun porphyry copper deposit is located 100 km NE of Tabriz and 75 km NW of Ahar in northwestern Iran (46 45 35E, 38 38N) (Fig. 1). This deposit is one of the most important copper deposits associated with calc-alkaline intrusive rocks in the so-called Cenozoic Sahand-Bazman volcanic belt of Iran. This belt was formed as a result of subduction of the Arabian plate beneath central Iran during the Alpine orogeny (Asghari et al. 2009; Berberian and King 1981; Hezarkhani 2006). Sungun porphyries contain more than 500 Mt of sulfide ore, grading 0.76% Cu and ≈0.01% Mo (Hezarkhani and Wiliams-Jones 1998). The Oligo-Miocene Sungun porphyry was intruded as a sub-volcanic complex into upper Cretaceous carbonate rocks, a series of Eocene arenaceous–argillaceous rocks, and a series of Oligocene dacitic breccias, tuffs, and trachy-andesitic lavas. The Sungun deposit occurs as stocks and dikes, with composition from quartz monzodiorite through quartz monzonite and granodiorite to granite (Calagari 2004). This deposit displays features related to both porphyrtic and skarn deposits (Karimzadeh 2004). Skarn-type alteration (and associated mineralization) is as a narrow layer along the eastern and northern margin of the stock in the Sungun valley (Mehrpartou 1993).

The Aras River forms the border between Iran and Armenia and Azerbaijan and lies approximately 40 km north of the mine. The Aras River flows in a northeasterly direction to reach the Caspian Sea some 200 km to the east. Two major river systems, the Illgineh and the Zarnekab, are also located in this area. The Sungun copper mine lies within the catchment area of the Illgineh River, while the tailing dam and impoundment area lie within the catchment area of the Zarnekab River. Illgineh is the main stream in the mine area; sub-streams include Sungun chay, Pakhir chay, Miyankafe, and Khoineroad, which all ultimately flow into the Illgineh River.

Materials and Methods

Sediment Sampling

Sediment samples were collected in May 2008. A judgmental approach was used to select sampling sites, because random sampling is often uneconomical and time consuming in industrially contaminated areas. At least 1 kg of sediment was taken from 44 stations at depths of 0–5 cm, using a plastic device to avoid possibly contaminating the samples with metals. Sampling points are shown in Fig. 2. Sediment samples were collected from the riverbanks, moving from upstream to downstream of the selected rivers. The collected samples were put in polyethylene bags and were immediately sent to the laboratory where they were air-dried at room temperature, sieved through 64 μm mesh size, and stored in polyethylene plastic containers. Elemental concentrations of sediment samples were measured using ICP-MS/OES at the Labwast laboratory, Australia. The digestion procedure includes adding HCl + HNO3 + HF into the sample, running it through a microwave at high temperature and pressure conditions, and finally adding boric acid solution to complex free fluoride and re-dissolve precipitates. This method yields near-total dissolution, and achieves good recoveries for the most resistive minerals. Precision was checked using replicate samples. The mean relative standard deviation ranged from 1.80 for Se to 4.50 for Cd. The analytical quality and measured values for both total and extracted concentrations of metals were verified by analyzing a blank sample (containing only the reagents), standards, and certified reference materials (STD TMDA-70), and by duplicate samples in each analytical series.

Sequential Extraction Method

Eleven sediment samples were chosen for BCR sequential extraction, based on total concentration of the targeted elements and a background sample. Fractionation pattern in the samples was evaluated using the BCR three step sequential extraction procedure (Iskandar and Kirkham 2000; Lacala et al. 2003, Rao et al. 2008; Ure et al. 1993). Each chemical fraction was determined as follows:

Exchangeable (F1): 50 mL of 0.11 M acetic acid (CH_3COOH) was added to 1 g of air dried sieved sediment sample in a polypropylene tab and shaken for 16 h at room temperature.

Contaminants bound to iron and manganese oxides (F2) were extracted by adding 50 mL of 0.1 M hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) (adjusted to pH 2) onto the residue from fraction 1 with continuous shaking for 16 h.

Elements bound to organic matter and sulfides (F3): 10 mL of 8.8 M hydrogen peroxide (H_2O_2) was added to the residue from the F2 step. The tubes were covered and

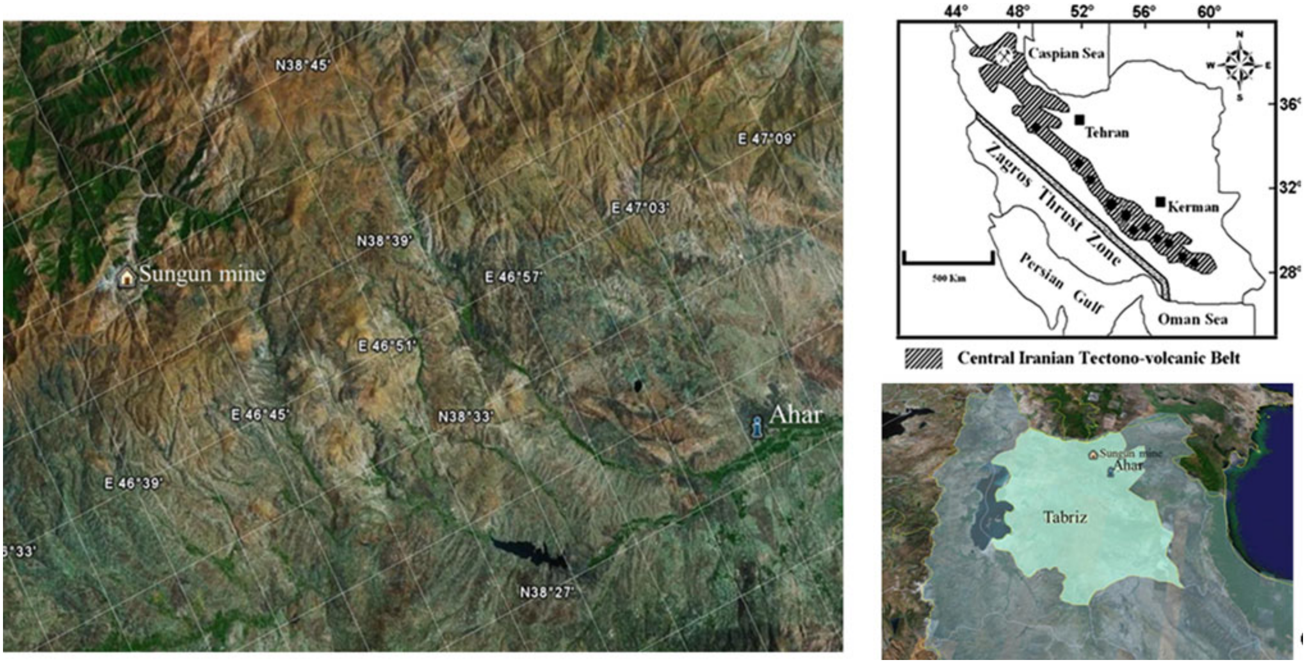

Fig. 1 Cenozoic Sahand–Bazman volcanic belt and location of the Sungun mine

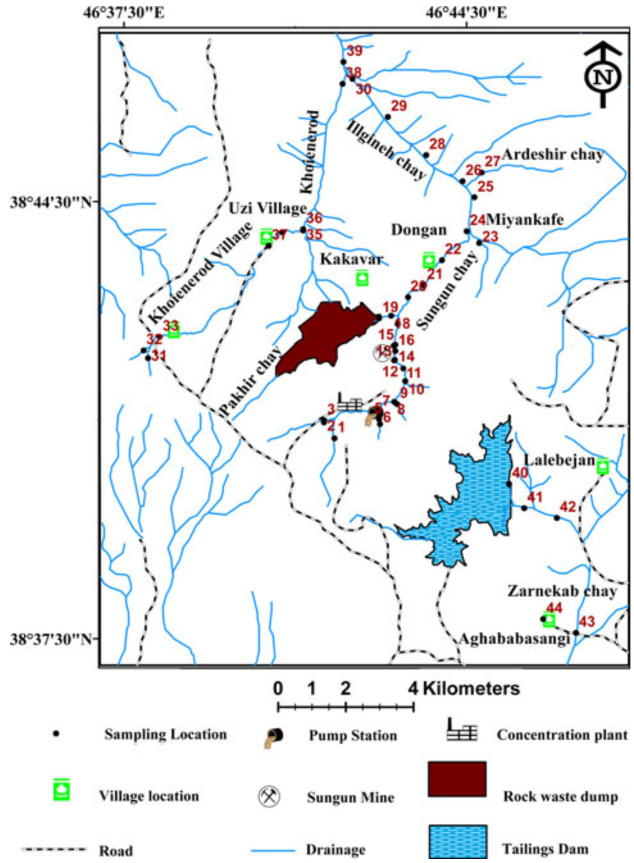

Fig. 2 Location of sediment sampling points (pump station and concentrate plant is in the Sungun chay (upstream of Illgineh River), rock waste is in the Pakhir chay (midstream of the Illgineh River), and the tailings dam is in the upstream section of the Zarnekab River)

the contents digested for 1 h at room temperature with occasional manual shaking and 1 h at 85°C in a water bath. Then, the volume was reduced to around 2–3 mL by further heating. After cooling, 50 mL of 1.0 M ammonium acetate solution (CH_3COONH_4) (adjusted to pH 2 by adding HNO_3) was added to the residue. The sample solution was shaken as described in Step 1.

Residual fraction (F4): The residue from F3 step was extracted by adding a mixture of 30 mL hydrochloric acid and 10 mL nitric acid (ratio $3HCL:1HNO_3$).

After completing each step, the extracted phases were separated from the solid phase by centrifugation at 2,500 rpm for 30 min. The supernatant was then filtered through a 0.45 μm filter (ALBET, Nitrato Celulosa), keep in dark glass bottles and stored at 4°C until analysis. Extracted solutions were sent to the ACME laboratory, Canada, where the concentrations of trace elements (As, Se, Cr, Co, Cd, Ni, and Zn) were determined using ICPMS. The accuracy of the sequential extraction method was evaluated from the elemental recovery after the entire extraction procedure. The recovery percentage for each element in each sediment sample was calculated by comparing the sum of the four fractions with the total concentration. The percent recoveries of As, Se, Cr, Co, Cd, Ni, and Zn were 108.45, 117.8, 65.73, 110.45, 96.82, 96.27, and 115.8%, respectively.

Assessment of Sediment Contamination Intensity

The enrichment factor (EF) is often used to evaluate anthropogenic inputs in sediment. EF is calculated by comparing the concentration of an element with a reference element. Common reference elements include Sc, Mn, Ti, Al, Zr, Sr, and Fe (Cevik et al. 2009; Eby 2004; Hernandez et al. 2003; Liu et al. 2009; Wang et al. 2008). The following formula is generally used to calculate the EF

$$\mathrm{EF} = \frac{\left(\frac{\mathrm{M}}{\mathrm{RM}}\right)_{\mathrm{Sample}}}{\left(\frac{\mathrm{M}'}{\mathrm{RE}}\right)_{\mathrm{Background}}}$$

where M is the concentration of the target element in sample, M′is the concentration of the target element in background, and RE is the reference element in both sample and background.

In this study, Al was chosen as the reference element, because it was assumed that the Al in the sediments was mainly associated with natural sources. The uncontaminated sediment from natural drainages (sample S-3) was taken as background since it was not affected by anthropogenic sources. According to Sutherland (2000), five contamination classifications can be recognized, based on the enrichment factor:

EF < 2 deficiency to mineral enrichment
EF = 2–5 moderate enrichment
EF = 5–20 significant enrichment
EF = 20–40 very high enrichment
EF > 40 extremely high enrichment

Singh et al. (2002) developed the concept of a sediment pollution index (SPI). SPI is a multi-metal method for assessing sediment quality by considering trace metal concentrations and potential metal toxicity. SPI was determined using the following equation:

$$\mathrm{SPI} = \sum\left(\mathrm{CE_m} \times \mathrm{W_m} \Big/ \sum \mathrm{W_m}\right)$$

$$\mathrm{CF_m} = \mathrm{M_x}/\mathrm{M_b}$$

where $\mathrm{CF_m}$ is the ratio of mean metal concentration ($\mathrm{M_X}$) in the sediment to background value ($\mathrm{M_b}$), $\mathrm{W_m}$ is toxicity weight, and $\mathrm{W_m}$ is for Cr = 2, Zn = 1, Ni = 5, Cd = 30, As = 10 (Lin et al. 2008; Yang et al. 2009). The following SPI categories are recognized:

SPI < 2 natural sediment
SPI = 2–5 low polluted sediment
SPI = 5–10 moderately polluted sediment
SPI = 10–20 highly polluted sediment
SPI > 20 dangerous sediment

Results and Discussion

Trace Metal Concentration

Table 1 shows total concentrations of As, Se, Cr, Co, Cd, Ni, and Zn in the surface sediments. The mean concentration distribution displays the following order: Zn > Cr > Ni > As > Co > Se > Cd. Contaminant levels in sediment samples, the average metal concentration for continental shale (Turekian and Wedepohl 1961), and background values are also provided in Table 1. The average concentration of Se and As in the sediments was much higher than the shale and background values, while the concentration of Ni, Cr, Zn, Cd, and Co was close to background values, indicating little enrichment of these metals. Chromium, Ni, and Co concentrations in the Illgineh River sediment were lower than in the Zarnekab River sediment, while As, Zn, Cd, and Se concentrations in the sediment of Illgineh River were higher. These results indicate the different natural sources of elements near the Sungum mine, because these sediments were not contaminated by anthropogenic inputs.

Sediment quality guidelines (SQGs) are commonly used to evaluate potential ecological effects of contaminated sediment. For this purpose, MacDonald et al. (2000) suggested two consensus-based SQGs, threshold effect concentration (TEC) and probable effect concentration (PEC). TECs are values below which harmful effects on sediment dwelling organisms are not expected. PECs are values above which harmful effects on sediment-dwelling organisms are expected to occur frequently. In this study, trace metal concentrations in sediments of the Sungun mine were compared to the consensus-based TEC and PEC values (Table 1). Chromium, Ni, Cd, and Zn concentrations were below the PEC, while As was much higher than the PEC.

Variations of SPI and average value of EF along the course of the rivers are displayed in Figs. 3 and 4. The EF results are given in Table 2. The EF for Ni and Cr are less than 2 over the entire course of the two rivers, showing that the sediment is not significantly contaminated by Ni and Cr. In contrast, Zn in S-18 and S-19 (Pakhir chay) of the Illgineh River sediments is significantly enriched, with an EF value of 6, while Sungun mine sediments was not enriched in Zn. The EF of Co was 1 in river sediment of the Sungun mine, showing no enrichment of this metal, except in the tailings dam sample (S-40) (Fig. 2). The EF of Cd in the S-18, S-19 (Pakhir chay), and S-12 (a tunnel below the mine pit) sediment samples was 3.5, 3, and 4, respectively, reflecting moderate anthropogenic contamination. Generally, the EF for Cd was less than 1 in the river sediments

Table 1 Trace metal concentration (in mg/kg, except for Al) in Sungun mine sediments compared with mean metal concentrations and sediment quality guidelines (S-1 to S-39 from Illgineh and S-40 to S-44 from Zarnekab River)

Sample	Ni	Zn	Cr	Al (%)	Co	Cd	As	Se	pH
S-1	57.0	126.5	101.0	8.21	22.5	0.5	20.0	0.4	7.9
S-2	86.0	119.7	123.0	7.10	17.7	0.2	138.7	0.3	7.2
S-3	42.0	126.1	73.0	7.44	19.2	0.7	15.1	1.1	7.9
S-4	54.0	86.0	81.0	7.20	19.3	0.3	12.8	1.0	7.1
S-5	50.0	36.1	66.0	7.69	26.9	0.2	25.7	8.7	7.8
S-6	63.0	82.6	65.0	7.22	35.3	0.4	20.9	6.8	7.9
S-7	61.0	142.4	77.0	7.39	23.2	0.5	32.0	3.2	7.7
S-8	53.0	142.6	71.0	7.72	24.1	0.5	34.6	3.2	8
S-9	38.0	110.3	64.0	7.06	15.1	0.3	13.7	0.4	8.1
S-10	69.0	96.1	57.0	6.86	34.6	0.4	29.0	6.7	7.1
S-11	64.0	92.7	59.0	6.56	32.0	0.5	27.3	6.6	7.7
S-12	22.0	71.7	12.0	2.68	7.3	1.0	15.6	9.4	5.7
S-13	63.0	82.7	55.0	6.80	32.9	0.5	27.7	7.9	7.6
S-14	58.0	84.6	58.0	6.90	28.7	0.4	25.0	5.8	8
S-15	30.0	49.0	69.0	8.28	7.9	0.3	250.4	8.3	8.1
S-16	37.0	63.2	50.0	6.49	16.9	0.3	143.0	7.4	8.2
S-17	53.0	86.6	54.0	7.02	25.4	0.4	28.3	5.1	8.2
S-18	71.0	729.8	61.0	7.49	26.4	2.2	57.4	4.3	8
S-19	59.0	747.0	62.0	7.38	24.2	2.2	59.0	4.5	7.7
S-20	57.0	129.1	59.0	6.46	29.4	0.7	40.1	6.1	8
S-21	56.0	131.9	55.0	6.16	27.0	0.6	39.1	5.1	7.9
S-22	42.0	183.2	49.0	7.22	19.6	0.8	41.5	3.4	8
S-23	38.0	108.4	68.0	7.21	18.1	0.3	26.5	0.4	8
S-24	44.0	139.0	59.0	6.51	19.7	0.6	35.0	3.0	7.8
S-25	52.0	135.9	98.0	6.34	24.2	0.5	48.5	1.4	8.1
S-26	42.0	113.8	72.0	5.06	24.1	0.5	42.6	1.3	8.2
S-27	62.0	134.1	125.0	7.39	28.6	0.4	112.5	0.4	8.3
S-28	49.0	130.2	94.0	5.71	23.9	0.5	47.4	1.5	8
S-29	50.0	122.9	99.0	6.28	23.6	0.4	46.5	1.1	8.1
S-30	50.0	124.5	90.0	5.50	24.8	0.5	45.2	1.3	8
S-31	41.0	109.2	84.0	8.04	15.2	0.8	11.7	0.5	7.7
S-32	40.0	87.3	76.0	8.23	15.4	0.5	10.8	0.5	7.7
S-33	40.0	99.3	76.0	7.34	14.4	0.5	10.2	0.5	7.5
S-34	38.0	79.5	88.0	6.78	15.9	0.3	18.0	0.5	8
S-35	40.0	89.9	84.0	7.10	17.7	0.3	29.1	0.3	8.4
S-36	45.0	82.2	94.0	7.14	17.2	0.3	19.3	0.4	8.2
S-37	30.0	73.8	61.0	8.09	14.2	0.3	12.4	0.5	8
S-38	3.0	3.8	97.0	6.88	1.4	0.1	1.5	< 0.05	7.9
S-39	43.0	114.0	94.0	6.65	22.1	0.4	36.1	0.9	8
S-40	88.0	52.3	44.0	5.95	51.7	0.2	17.6	10.7	8.5
S-41	74.0	110.2	119.0	7.17	17.0	0.5	15.5	0.4	7.2
S-42	43.0	99.3	89.0	7.81	17.6	0.3	16.3	0.4	8
S-43	38.0	83.0	94.0	7.20	16.2	0.2	13.0	0.4	8.2
S-44	62.0	83.9	151.0	7.09	19.6	0.1	10.2	0.3	8.3
Mean	49.93	129.46	76.75	–	21.78	0.51	39.15	3.07	7.8
Minimum	3	3.8	12	2.68	1.4	0.1	1.5	0.2	5.7
Maximum	88	747	151	8.28	51.7	2.33	250.4	10.74	8.5
SD	15.7	138.2	24.9	0.96	8.4	0.41	44.3	3.1	–

Table 1 continued

Sample	Ni	Zn	Cr	Al (%)	Co	Cd	As	Se	pH
Shale[a]	68	95	90	–	19	0.3	13	0.6	–
Background value[b]	42	126.1	73.00	7.44	19.2	0.73	15.1	1.14	–
Threshold effect concentration[c]	22.7	121	43.4	–	0.99		9.8	–	–
Probable effect concentration[c]	48.6	459	111	–	4.98		33	–	–

[a] The world average concentration of shale (Turekian and Wedepohl 1961)

[b] Uncontamination sediment sample (S-3)

[c] MacDonald et al. (2000)

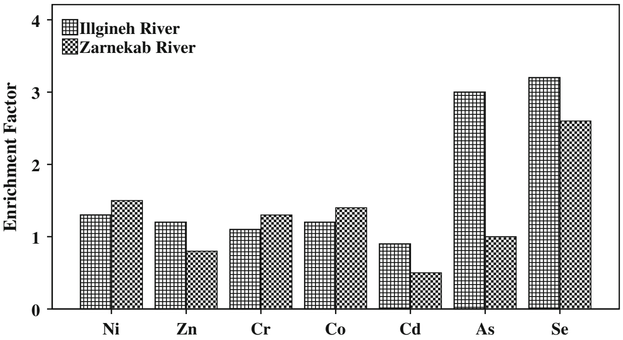

Fig. 3 Average enrichment factor values for sediments of Illgineh and Zarnekab Rivers

down-gradient of the Sungun mine, showing no enrichment of this element.

Arsenic was moderately enriched in most sediment samples of the Illgineh River, but was not enriched in the Zarnekab River sediment samples. Arsenic pollution in S-27 (Ardeshir chay) and S-2 (natural spring) samples is due to geogenic or natural sources, because these samples are not affected by anthropogenic sources.

Selenium has the highest EF values among the analyzed elements. The highest Se EF values occurred in S-3 (a tunnel below the mine pit). Illgineh River sediments also showed very high Se enrichment, and the Sungun mine sediment samples were also moderately enriched in Se (mean EF 3.17). Selenium concentration in volcanic rocks around Sungun mine is mainly around 0.5 mg/kg, which is higher than the bulk crust continental concentration (0.13 mg/kg) of this element. Therefore, the enrichment of Se in sediment is mainly associated with relatively high natural concentration of Se in this area.

The calculated EF values for Cd, Zn, Se, and As in the sediment samples of the Illgineh River was higher than that of the Zarnekab River, while the EF for Ni, Cr, and Co of the Illgineh River sediment was lower than in the Zarnekab River. These differences in enrichment values are associated with the natural occurrences of trace elements in Zarnekab River basin as well as the contamination of Illgineh River sediments by anthropogenic sources, such as effluents from the mineral dressing plant, rock waste drainages, and a portion of the tailings. The EF values for Ni, Zn, Cr, Co, Cd, As, and Se in the tailing waste were 2.6, 0.5, 0.8, 3.4, 0.4, 1.5, and 11.8 (S-40). The EF values for Ni, Zn, Cr, Co, Cd, As, and Se in the effluents discharging of concentrate plant were 1.35, 0.48, 0.90, 1.62, 0.40, and 1.54 (S-4 and S-5). EF displayed the following decreasing trend in the sediments: Se > As > Ni > Co > Cr > Zn > Cd.

The SPI value for Ni, Cr, Co, Cd, Zn, Se, and As varied between 0.57 and 3.83 in the Illgineh River

Fig. 4 Sediment pollution index variations for sediments in Illgineh and Zarnekab Rivers (S-1 to S-39 from Illgineh River, and S-40 to S-44 from Zarnekab River)

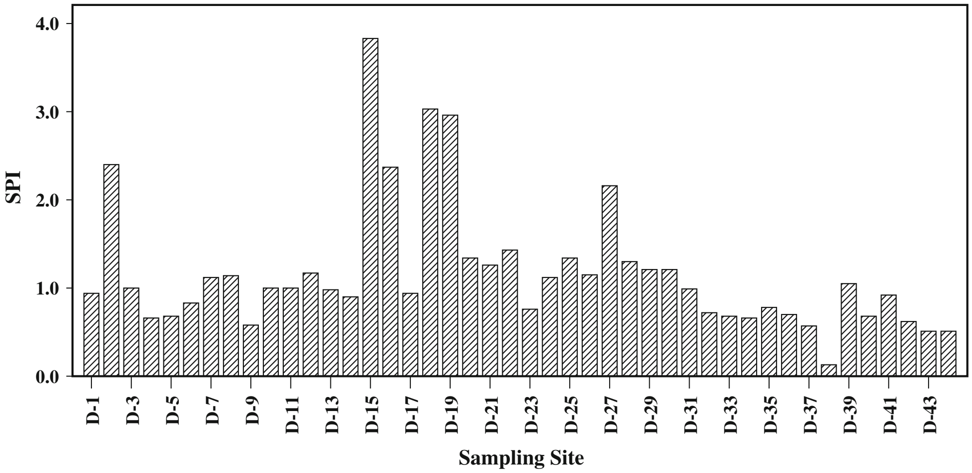

Table 2 Calculated enrichment factors for trace metals in surficial sediments (S-1 to S-39 for Illgineh and S-40 to S-44 for Zarnekab River)

Site	Sampling location	Ni	Zn	Cr	Co	Cd	As	Se
S-1	Sungun chay	1.2	0.9	1.3	1.1	0.6	1.2	0.3
S-2	Spring	2.1	1.0	1.8	1.0	0.3	9.6	0.3
S-3	Drainage	1.0	1.0	1.0	1.0	1.0	1.0	1.0
S-4	Sungun chay before waste plant concetrate	1.3	0.7	1.1	1.0	0.5	0.9	0.9
S-5	Sungun chay after waste plant concetrate	1.2	0.3	0.9	1.4	0.3	1.6	7.3
S-6	Sungun chay after waste plant concetrate	1.5	0.7	0.9	1.9	0.6	1.4	6.1
S-7	Sungun chay	1.5	1.1	1.1	1.2	0.7	2.1	2.9
S-8	Sungun chay	1.2	1.1	0.9	1.2	0.7	2.2	2.7
S-9	Drainage	1.0	0.9	0.9	0.8	0.4	1.0	0.3
S-10	Sungun chay	1.8	0.8	0.8	2.0	0.7	2.1	6.4
S-11	Sungun chay	1.7	0.8	0.9	1.9	0.8	2.0	6.5
S-12	Tunnel below pit mine	1.5	1.6	0.5	1.1	3.9	2.9	23.0
S-13	Sungun chay	1.6	0.7	0.8	1.9	0.7	2.0	7.6
S-14	Sungun chay	1.5	0.7	0.9	1.6	0.6	1.8	5.5
S-15	First exploration tunnel	0.6	0.3	0.8	0.4	0.4	14.9	6.6
S-16	Sungun chay(after first exploration tunnel)	1.0	0.6	0.8	1.0	0.5	10.9	7.4
S-17	Sungun chay before Pakhir chay junction	1.3	0.7	0.8	1.4	0.6	2.0	4.7
S-18	Pakhir chay before Sungun chay junction	1.7	5.8	0.8	1.4	3.0	3.8	3.7
S-19	Pakhir chay after waste dump	1.4	6.0	0.9	1.3	3.0	3.9	4.0
S-20	Sungun chay after Pakhir chay junction	1.6	1.2	0.9	1.8	1.1	3.1	6.1
S-21	Sungun chay	1.6	1.3	0.9	1.7	1.0	3.1	5.4
S-22	Sungun chay before miyankafe chay junction	1.0	1.5	0.7	1.1	1.1	2.8	3.1
S-23	Miyankafe chay before sungun chay junction	0.9	0.9	1.0	1.0	0.4	1.8	0.3
S-24	Illgineh chay (after sungun chay and miyankafe chay junction)	1.2	1.3	0.9	1.2	0.9	2.7	3.0
S-25	Illgineh chay before ardashir chay junction	1.5	1.3	1.6	1.5	0.9	3.8	1.4
S-26	Illgineh chay after ardashir chay junction	1.5	1.3	1.5	1.8	0.9	4.2	1.6
S-27	Ardeshir chay	1.5	1.1	1.7	1.5	0.6	7.5	0.3
S-28	Illgineh chay	1.5	1.3	1.7	1.6	0.9	4.1	1.7
S-29	Illgineh chay	1.4	1.2	1.6	1.5	0.7	3.6	1.2
S-30	Illgineh chay before khoinehroad junction	1.6	1.3	1.7	1.7	0.9	4.1	1.6
S-31	Khoinheroad	0.9	0.8	1.1	0.7	1.0	0.7	0.4
S-32	Khoinheroad	0.9	0.6	0.9	0.7	0.6	0.6	0.4
S-33	Khoinheroad	1.0	0.8	1.1	0.8	0.6	0.7	0.4
S-34	Khoinheroad before doroash junction	1.0	0.7	1.3	0.9	0.5	1.3	0.5
S-35	Doroash before khoinheroad junction	1.0	0.7	1.2	1.0	0.4	2.0	0.3
S-36	Khoinheroad after doroash junction	1.1	0.7	1.3	0.9	0.4	1.3	0.4
S-37	Khoinheroad	0.7	0.5	0.8	0.7	0.4	0.8	0.4
S-38	Khoinehroad before Illgineh chay junction	0.1	0.0	1.4	0.1	0.1	0.1	0.0
S-39	Illgineh chay after khoinehroad junction	1.1	1.0	1.4	1.3	0.7	2.7	0.9
S-40	Tailing waste	2.6	0.5	0.8	3.4	0.4	1.5	11.8
S-41	Tailings dam leakage	1.8	0.9	1.7	0.9	0.7	1.1	0.4
S-42	Zarnekab chay	1.0	0.8	1.2	0.9	0.3	1.0	0.3
S-43	Zarnekab chay	0.9	0.7	1.3	0.9	0.3	0.9	0.3
S-44	Aghababsangi village stream	1.2	0.9	1.3	1.1	0.6	1.2	0.3

sediments, and gradually decreased downstream. The stream sediment in the Illgineh River is classified as natural sediments, with no ecological risk. The calculated SPI for the same elements ranged between 0.5 and 0.92 in the Zarnekab River sediment. Therefore, they also pose no ecological risk.

Table 3 Ranges of trace metal concentration (mg/kg) in various fractions of surface sediments from the Sungun mine (F1: Exchangeable fraction, F2: Fe–Mn oxid fraction, F3: Oraganic matter/sulphide fraction, and F4: Residual fraction)

Element	Fraction	S-2	S-3	S-5	S-15	S-18	S-24	S-27	S-30	S-31	S-40	S-43
As	F1	0.16	0.08	0.15	1.4	0.00	0.09	0.39	0.06	0.36	0.20	0.16
	F2	70.78	1.77	10.95	65.0	3.76	6.52	10.97	5.38	2.02	7.36	3.08
	F3	26.21	1.11	6.90	19.8	0.95	3.12	6.24	3.16	1.59	6.49	1.59
	F4	56.78	15.42	11.45	157.5	50.43	26.42	117.25	43.65	10.05	8.80	4.30
Cd	F1	0.05	0.21	0.11	0.07	0.00	0.27	0.16	0.17	0.27	0.08	0.08
	F2	0.09	0.42	0.05	0.1	1.19	0.27	0.26	0.19	0.41	0.04	0.08
	F3	0.04	0.09	0.02	0.05	0.24	0.06	0.05	0.06	0.09	0.03	0.02
	F4	0.05	0.11	0.03	0.03	0.21	0.03	0.06	0.06	0.10	0.03	0.04
Co	F1	0.33	1.11	2.08	2.4	0.01	1.75	0.73	1.33	0.99	1.03	0.42
	F2	6.84	12.47	4.79	4.2	20.95	12.02	17.84	8.89	8.44	10.75	7.65
	F3	1.40	1.78	5.96	0.6	1.17	1.84	2.11	1.75	1.89	6.38	1.63
	F4	8.08	7.58	13.82	2.2	6.88	7.87	11.67	13.83	6.67	40.32	7.58
Cr	F1	0.58	0.41	1.42	0.4	0.00	0.56	0.62	0.65	0.43	2.88	0.50
	F2	3.96	4.67	16.32	12.3	8.23	6.23	5.94	4.65	4.88	9.98	4.05
	F3	8.71	6.80	4.76	5.3	3.33	4.27	7.95	4.60	8.94	3.93	5.73
	F4	60.13	40.48	9.29	55.9	44.29	27.70	66.02	35.07	48.41	5.72	41.21
Ni	F1	2.46	2.93	2.66	3.1	0.05	3.23	3.50	2.10	1.28	1.98	2.46
	F2	8.95	14.32	8.54	6.3	26.32	11.85	15.08	10.45	7.87	15.10	9.12
	F3	10.47	7.29	10.14	2.7	3.32	5.16	7.70	4.76	7.24	9.90	6.02
	F4	47.87	24.33	26.23	16.7	25.54	17.04	37.74	31.13	29.13	60.01	21.30
Se	F1	0.02	0.00	0.11	0.06	0.00	0.04	0.04	0.03	0.00	0.15	0.02
	F2	0.10	0.05	0.70	0.1	0.38	0.38	0.08	0.09	0.12	0.54	0.19
	F3	0.15	0.10	6.08	2.4	0.65	1.02	0.16	0.26	0.26	4.11	0.21
	F4	0.05	0.22	2.26	8.0	3.48	2.09	0.17	1.17	0.17	8.44	0.04
Zn	F1	12.34	13.89	7.15	9.5	0.42	17.89	9.40	12.66	10.81	10.86	7.65
	F2	47.25	35.79	20.07	18.2	358.47	50.57	37.98	41.61	33.59	31.24	24.11
	F3	17.93	18.56	8.23	5.1	66.42	21.90	17.54	19.31	19.50	11.42	14.43
	F4	43.14	88.26	7.79	20.0	342.55	50.51	103.52	75.32	58.70	7.03	52.79

Chemical Speciation of Trace Elements in Sediment

Table 3 shows the sequential extraction results for the studied trace elements in the Sungun mine sediment samples. The mean concentrations (%) for the extraction steps and residuals (determined using the BCR sequential extraction procedure) are displayed in Fig. 5. On average, only 10% of the As, Se, Ni, Cr, Co, and Zn were extracted in the exchangeable fraction, while a high percentage (over 30%) of the Cd was exchangeable, which was due to the high concentration of carbonates in the sediments. $CdCO_3$ is easily formed at neutral pH and is sensitive to environmental conditions such as pH. When pH decreases, Cd bound to carbonate is released into the water, thus causing pollution (Balistrieri et al. 2007). Generally, the exchangeable fraction is assumed to be bioavailable to organisms living in the sediments (Owor et al. 2007). Overall, the speciation of Cd in the sediments from Sungun mine exhibited high bioavailability; consequently, this element poses a high potential risk to the aquatic ecosystem.

Twenty-two per cent of the As, 43% of the Co, 17% of the Cr, 24% of the Ni, 15% of the Se, 42% of the Cd, and 34% of the Zn exist in the Fe–Mn oxides phase (F2). So, the release of these contaminants into the water is limited by their adsorption to Fe–Mn oxy-hydroxides. Under reducing conditions, decomposition of Fe and Mn oxides would remobilize Fe^{3+} and Mn^{4+} (Passos et al. 2010). Also, acidification of sediments by anthropogenic input can decrease the retention of metals by the oxide fractions (e.g. Al, Fe, and Mn oxides) in the pH ranges below the point of zero charge (Wilkens and Loach 1997).

Relatively low percentages (9.24–13.85%) of six trace elements (As, Cd, Co, Ni, Zn, and Cr) were found in the

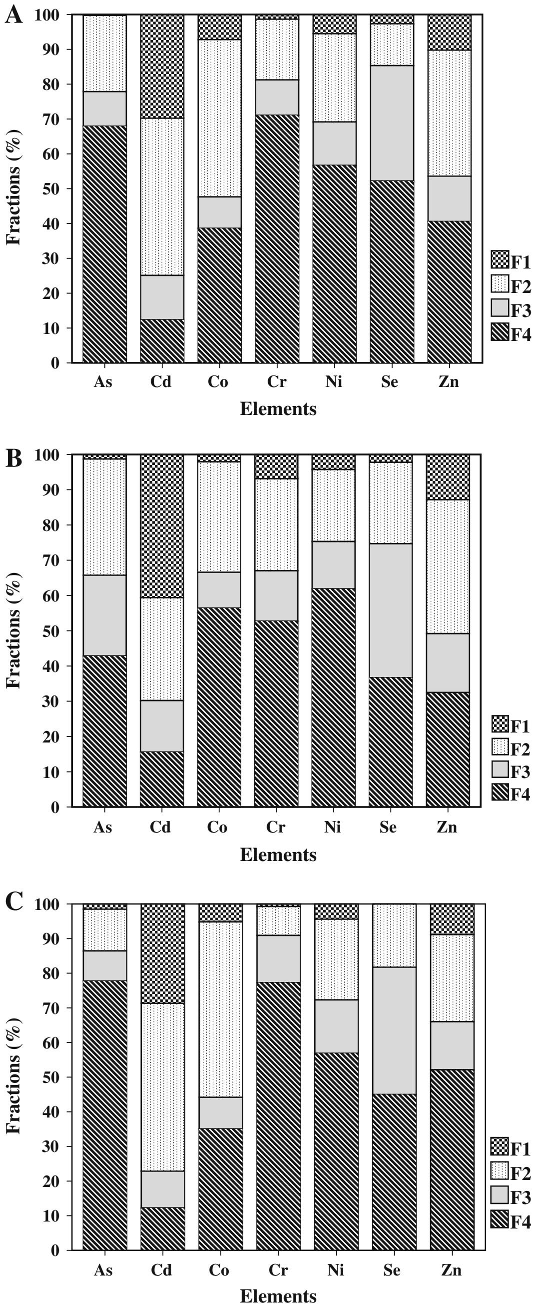

Fig. 5 Partitioning of speciation of trace metals in surface sediments of the Sungun mine (**a**: Illgineh River, **b**: Zarnekab River, **c**: background sample)

organic and sulfide phases (Step 3). However, 34% of the Se was contained in the organic and sulfide fraction. The results from the total concentration studies indicate that the Se was adsorbed by organic matter (Kabata-Pendias and Mukherjee 2007). Under oxidizing conditions, contaminants present in this fraction may be remobilized into the aquatic environment. In general, organically-bound trace metals are often more phytoavailable than other fractions (Stevenson 1991).

All studied contaminants, except Cd (65% of the As, 41% of the Co, 68% of the Cr, 57% of the Ni, 48% of the Se, and 41% of the Zn), were contained in the residual fraction. These are most likely of natural origin and would not be expected to be remobilized into the local aquatic environment, except over very long time scales (Forghani et al. 2009; Zhigang 2008).

Table 4 indicates the contaminant concentration in the non-residual and residuals fraction in the Sungun mine sediment. High values of Cd associated with the non-residual fractions show that it could be transferred into the food chain through water reservoirs. The highest residual phase concentrations of As, Se, Cr, Cd, and Zn was in the Illgineh River sediment, while the highest residual fraction concentration for Ni and Co was found in the Zarnekab River sediment.

The average order of decreasing potential trace metal mobility in the sediments of the Sungun mine was Cd > Co > Zn > Se > Cr > Ni > As. The mobility and potential bioavailability for plant uptake decreases in the approximate order of the sequential extraction sequence (Lottermoser et al. 1999). Trace contaminants in absorptive sites of stream sediments are most available to fluvial organisms.

Conclusions

This study indicates that the geo-environmental behavior of most of the studied trace elements in the sediments near the Sungun porphyry copper mine is controlled by their natural sources. Investigation of trace elements (As, Se, Ni, Cr, Cd, Co, and Zn) in the sediment around the Sungun copper mine show that only As and Se were apparently elevated, but that the concentration of As and Se was high in some samples due to lithogenic sources. The elements Cd, Zn, As, and Se were found to be enriched in the Illgineh River sediments. The EF values for Cr, Ni, and Co were high in the Zarnekab River sediments. However, the sediments in both rivers were classified as natural sediment, without ecological risk, because the residual fraction dominated and the contaminant concentrations were low. The enrichment factor in the studied sediments, from highest to lowest, were Se > As > Ni > Co > Cr > Zn > Cd. Most of the contaminated samples were associated with rock waste drainages, tailings waste, and natural sources. The sequential extraction indicates that the Cd is potentially highly mobile; given its biological availability for living organisms, it may pose long-term risks for bioaccumulation in the Sungun mine aquatic system. The main fraction of As, Se, Cr, Co, Zn, and Ni in sediments was associated with the residual fraction, which has minimal bioavailability.

Table 4 Trace metal concentrations (mg/kg) in non-residual (NR) and residual (R) fraction in sediment of the Sungun mine

Site	As	R	Cd	R	Co	R	Cr	R	Ni	R	Se	R	Zn	R
	NR		NR		NR		NR		NR		NR		NR	
S-2	21.0	36.9	26.1	21.6	17.2	48.5	6.0	81.9	10.5	68.6	28.0	15.9	21.4	35.8
S-3	5.4	83.9	28.9	13.4	22.3	33.0	7.6	77.3	16.7	49.8	13.6	59.3	14.5	14.5
S-5	20.4	38.9	28.7	13.8	16.0	51.9	23.6	29.2	14.9	55.2	25.1	24.7	27.3	18.0
S-15	11.8	64.6	30.3	9.0	25.6	23.1	8.2	75.5	14.1	57.8	8.3	75.1	20.8	37.7
S-18	2.8	91.5	29.0	13.0	25.4	23.7	6.9	79.3	17.9	46.2	7.6	77.1	18.5	44.6
S-24	9.0	73.1	31.8	4.5	22.2	33.5	9.5	71.5	18.1	45.7	13.6	59.1	21.4	35.9
S-27	4.4	86.9	29.3	12.0	21.3	36.1	6.0	82.0	13.7	58.9	20.7	38.0	12.8	61.5
S-30	5.5	83.5	29.1	12.6	15.5	53.6	7.3	78.0	11.9	64.3	8.2	75.5	16.5	50.6
S-31	9.5	71.6	29.6	11.1	21.0	37.1	7.6	77.3	12.0	64.0	23.1	30.7	17.4	47.9
S-40	20.5	38.5	28.8	13.5	10.4	68.9	24.9	25.4	10.3	69.0	12.1	63.8	29.5	11.6
S-43	17.6	47.2	27.5	17.6	18.7	43.9	6.7	80.0	15.1	54.8	30.1	9.6	15.6	53.3

Acknowledgments The authors appreciate the cooperation of the Research and Development Division of the Sarcheshmeh Copper Complex and the HSE administrator. We thank Sungun Copper Complex for financial support and access to sampling and analysis. We also thank the industrial advisor of the project, N. Pirouznia, who made valuable suggestions.

References

Asghari O, Hezarkhani A, Soltani F (2009) The comparison of alteration zones in the Sungun porphyry copper deposit, Iran (based on fluid inclusion studies). Acta Geol Pol 59:93–109

Balistrieri LS, Seal RR, Piatak NM, Paul B (2007) Assessing the concentration, speciation, and toxicity of dissolved metals during mixing of acid-mine drainage and ambient river water downstream of the Elizabeth Copper Mine, Vermont, USA. Appl Geol 22:930–952

Bell FG, Bullock SET, Hälbich TFJ, Lindsay P (2001) Environmental impacts associated with an abandoned mine in the Witbank Coalfield, South Africa. Int J Coal Geol 45:195–216

Berberian M, King GC (1981) Towards a paleogegraphy and tectonic evolution of Iran. Can J Earth Sci 18:210–265

Calagari AA (2004) Fluid inclusion studies in quartz veinlets in the porphyry copper deposit at Sungun, East-Azarbaidjan, Iran. J Asian Earth Sci 23:179–189

Cevik F, Goksu M, Derici O, Findik O (2009) An assessment of metals pollution in surface sediments of Seyhan dam by using enrichment factor, geoaccumulation index and statistical analysis. Environ Monit Assess 152:309–317

Eby GN (2004) Principles of environmental geochemistry. California Brooks/Cole-Thomson Learning, Pacific Grove

Forghani G, Moore F, Sanghoon L, Qishlaqi A (2009) Geochemistry and speciation of metals in sediments of the Maharlu Saline Lake, Shiraz, SW Iran. Environ Earth Sci 59:173–184

Gonzaleza E, Rodriguez MT, Sanchez JC, Espinosa AJF, Delarosa FJB (2000) Assessment of metals in sediments in tributary of Guadalquivir River (Spain) heavy metal partitioning and relation between the water and sediment system. Water Air Soil Pollut 121:11–29

Guo P, Song X, Duan T, Chen H (2007) Evaluation of a sequential extraction for the speciation of thorium in soils from Baotou area, Inner Mongolia. Talanta 71:778–783

Hernandez L, Probst A, Probst JL, Ulrich E (2003) Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. Sci Total Environ 312:195–212

Hezarkhani A (2006) Petrology of the intrusive rocks within the Sungun Porphyry Copper Deposit, Azerbaijan. Iran. J Asian Earth Sci 28:409–422

Hezarkhani A, Wiliams-Jones AE (1998) Controls of alteration and mineralization in the Sungun porphyry copper deposit. Iran Econ Geol 93:651–670

Iskandar IK, Kirkham MB (2000) Trace elements in soil: bioavailability, flux, and transfer. CRC Press LLC, Boca Raton

Kabata-Pendias A, Mukherjee A (2007) Trace element from soil to human. Springer, Berlin

Karimzadeh SA (2004) Garnet composition as an indicator of Cu mineralization: evidence from skarn deposits of NW Iran. J Geochem Explor 81:47–57

Lacala J, Silvaa MP, Garcıáb R, Sevilla MT, Procopioa JR, Hernandeza L (2003) Study of fractionation and potential mobility of metal in sludge from pyrite mining and affected river sediments: changes in mobility over time and use of artificial ageing as a tool in environmental impact assessment. Environ Pollut 124:291–305

Lin C, He M, Zhou Y, Guo W, Yang Z (2008) Distribution and contamination assessment of heavy metals in sediment of the Second Songhua River, China. Environ Monit Assess 137:329–342

Liu E, Shen J, Yang L, Zhang E, Meng X, Wang J (2009) Assessment of heavy metal contamination in the sediments of Nansihu Lake Catchment. China Environ Monit Assess 161:217–227

Lottermoser BG, Ashely PM, Lawie DC (1999) Environmental geochemistry of the Gulf Creek copper mine area, north eastern New South Wales. Aust J Environ Geol 39(1):61–74

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

Mehrpartou M (1993) Contributions to the geology, geochemistry, ore genesis and fluid inclusion investigations on Sungun CuMo porphyry deposit (northwest of Iran). PhD thesis, Hamburg University, Hamburg, Germany

Milenkovic N, Damjanovic M, Ristic M (2005) Study of heavy metal pollution in sediments from the Iron Gate (Danube River), Serbia and Montenegro. Pol J Environ Stud 14:781–787

Owor M, Hartwing T, Muwanga A, Zachmann D, Pohl W (2007) Impact of tailing from the kilembe copper mining district on lake George, Uganda. Environ Geol 51:1065–1075

Passos EA, Alves JC, Santos IS, Alves JHP, Garcia CAB, Costa ACS (2010) Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. Microchem J 96:50–57

Quevauviller PH (1998) Operationally defined extraction procedures for soil and sediment analysis: I. Standardization. Trends Anal Chem 17:289–298

Rao CRM, Sahuquillo A, Sanchez JF (2008) A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. Water Air Soil Pollut 189:291–333

Shiowatana J, Tantidanai N, Nookabkaew S, Nacapricha D (2001) A flow system for the determination of metal speciation in soil by sequential extraction. Environ Int 26:381–387

Singh M, Muller G, Singh IB (2002) Heavy metals in freshly deposited stream sediments of rivers associated with urbanization of the Ganga Plain, India. Water Air Soil Pollut 141:35–54

Stevenson FJ (1991) Organic matter macronutrient reactions in soil. In: Mortvedt JJ (ed) Micronutrients in Agriculture. SSSA, Madison, pp 145–186

Sutherland RA (2000) Bed sediment—associated trace metals in an urban stream, Oahu. Hawaii Environ Geol 39:611–627

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51:844–851

Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the earth's crust. Geol Soc Am Bull 72:175–192

Ure A, Quevauviller PH, Muntau H, Griepink B (1993) The speciation of heavy metals in soils and sediments: an account of the improvement and harmonization of extraction techniques undertaken under the auspices of Community Bureau of Reference (BCR). Int J Environ Anal Chem 51(135):139

Wang S, Cao Z, Lan D, Zheng Z, Li G (2008) Concentration distribution and assessment of several heavy metals in sediments of west-four Pearl River Estuary. Environ Geol 55:963–975

Wilkens BJ, Loach PG (1997) Accumulation of cadmium and zinc from diffuse emission on acid sandy soils, as a function of soil composition. Water Air Soil Pollut 95:1–16

Yang Z, Wang Y, Shen Z, Niu J, Tang Z (2009) Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. J Hazard Mater 166:1186–1194

Yuan C, Shi J, He B, Liu J, Liang L, Jiang G (2004) Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. Environ Int 30:769–783

Zemberyová M, Barteková J, Hagarová I (2006) The utilization of modified BCR three-step sequential extraction procedure for the fractionation of Cd, Cr, Cu, Ni, Pb and Zn in soil reference materials of different origins. Talanta 70:973–978

Zhigang Y (2008) Comparison between BCR sequential extraction and geo-accumulation method to evaluate metal mobility in sediments of Dongting Lake, Central China. Chin J Oceanol Limn 26:14–22