

# Metal pollution assessment of sediment and water in the Shur River

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**Abstract** Intensified industrialization and human activities have resulted in the release of various contaminants into the environment. Among them, heavy metals are often present as a result of mining, milling and industrial manufacturing. In the present investigation, bulk concentrations Pb, Cd, Zn, Cu, Fe, Ca and Al in Shur River (Iran) bed sediments and water around the Sarcheshmeh copper mine were measured from several sample locations. In addition, partitioning was assessed to determine the proportions of metals in different forms. The degree of sediment contamination was evaluated using an Enrichment Factor (EF) and geo-accumulation index ( $I_{geo}$ ) and a newly developed pollution index ( $I_{POLL}$ ). Elevated metals in sediment and water were found to be correlated with areas of the river that were proximal to direct and indirect mining activities. Cadmium and Zn showed the highest pollution index. Cluster analysis was performed in order to assess heavy metal interactions between water and sediment. Chemical partitioning studies revealed

that organic metallic bonds were not significantly present in the sediment of the Shur River.

**Keywords** Pollution · Assessment · Geochemistry · Sediment · Water · Elements · Index · Mine

## Introduction

In many aquatic systems, deposition of contaminants, including heavy metals, can lead to elevated sediment concentrations that have the potential to cause toxicity to aquatic biota (Yang and Rose 2003; Heyvart et al. 2000). Because of the importance of sediments to the overall quality of aquatic systems, sediment analysis is often included in environmental assessment studies (Adekola and Eletta 2007; Li et al. 2006; Jain et al. 2005; Horsfall and Spiff 2002). To evaluate the heavy metal burden in the environment, it is usually not sufficient to measure only total concentrations, but also to establish the proportions of heavy metals present in various, soluble fractions, which are commonly quantified by a sequential extraction procedure (Chester and Hughes 1967; Tessier et al. 1979, Forstner and Wittmann 1981; Horowitz et al. 1999; Stamatis et al. 2006). Sediments and suspended particulate matter (SPM) play an important role in the adsorption of dissolved heavy metals. They can also be a potential reservoir of metals, by releasing them to the water column under changing physical and chemical conditions (Karbassi et al. 2007). The levels of certain trace elements in rivers, lakes and other water systems have been found to be moderately, to very, high as a result of industry discharges (Al-Masri et al. 2002; Coker et al. 1995). It is known that sediments play a significant

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role in controlling the metal concentrations in many of these aquatic environments and therefore the behavior of metals, including sedimentation and resuspension, have attracted the attention of many researchers (Bellucci et al. 2003; Betroitto et al. 2003). Several sequential extraction and chemical portioning methods have been developed for speciation and determination of metal bonding in the particulate phase (Chester and Hughes 1967). It is generally believed that metals in carbonate, sulfide and organic compounds are more toxic due to higher bioavailability, and thus are more critical from an environmental risk assessment standpoint.

Heavy metal mining is an important industry in Iran. Many of the operating mines are near rivers which act as a source of water for human consumption and agriculture. Because of the importance of these rivers as a source of clean water, it is essential to closely investigate the potential metal load of the systems and the geochemical cycle of trace elements and their behavior in these regions of the country. Sarcheshmeh copper complex (SCC), the largest copper mine in Iran, is located 50 km from Rafsanjan City in Kerman Province. The mine ores include cooperite, malachite and azurite. The mine storage is estimated at 740 million tons. Open pit extraction is being practiced at the Sarcheshmeh copper mine and facilities such as the concentration plant, melting and molding are operating at the SCC. In the present investigation, the trace elements found in the bed sediments and water of the Shur River, located at the Sarcheshmeh copper mine, were studied.

The catchment area of the Shur River is approximately 200 km<sup>2</sup> and the discharge is about 0.53 m<sup>3</sup>/s. Since the climate of the surrounding area is arid, the Shur River is the most important source of potable water. The association of metals with various sedimentary phases was investigated in this study. The level of pollution associated with the study area was quantified using a geochemical index, enrichment factor and a new index developed during this research.

## Materials and methods

Riverine sediments were collected from 12 sample locations in the Shur River during the winter of 2005 using a Peterson grab sampler (Fig. 1). The river-bed sediments, which were brown to black in color, were air-dried and passed through a 63- $\mu$ m mesh (equivalent

to a No. 230 sieve, ASTM E-11). The sieved sediment was powdered using an agate mortar and pestle. About 0.5 g of the powdered sample was placed in a Teflon beaker containing 10 mL aqua regia. The mixture was heated until most of the liquid had evaporated, and allowed to cool before 5 mL of hydrogen fluoride (HF) were added. The samples were further cooled to room temperature before being filtered. The filtrates were transferred to 50 mL volumetric flasks and brought to volume with 1 N HCl. Chemical partition studies were conducted in four sequential steps: (1) acetic acid 25% v/v, (2) acetic acid 25% v/v-0.1 M hydroxylamine hydrochloride, (3) 30% H<sub>2</sub>O<sub>2</sub> "extraction with 1 M ammonium acetate" and (4) hot 50% HCl (Chester and Hughes 1967; Gibbs 1973). All the sample bottles and other containers were soaked in HNO<sub>3</sub> (10%) over night and rinsed with distilled water prior to use. Ten water samples were filtered through Whatman 0.45  $\mu$ m membrane filters (in order to examine the dissolved fraction), acidified (to pH<2) and stored at 40°C (Jain et al. 2005).

Trace metals (Cu, Zn, Cd, Pb, Ca, Fe and Al) were measured using a UNICAM flame atomic absorption spectrometer. Calibration curves were established using known standards. Procedural blanks and duplicates were run alongside the samples as part of the quality assurance program. The analytical accuracy was approximately  $\pm$ 3% for all elements. A standard sample (MESS-1) was analyzed using the same methods as an accuracy check. Analytical error was estimated to be  $\leq$ 4% (Table 1). Organic matter was estimated by recording the Loss on Ignition (LOI) of samples heated for 4 h at 450°C in a muffle furnace (Carver 1972).

The Weighted Pair Group method (GWP) was used to identify clustering tendencies among the samples (Davis 1973). To assess the intensity of metal contamination in Shur River sediments, the geochemical accumulation index was calculated using:

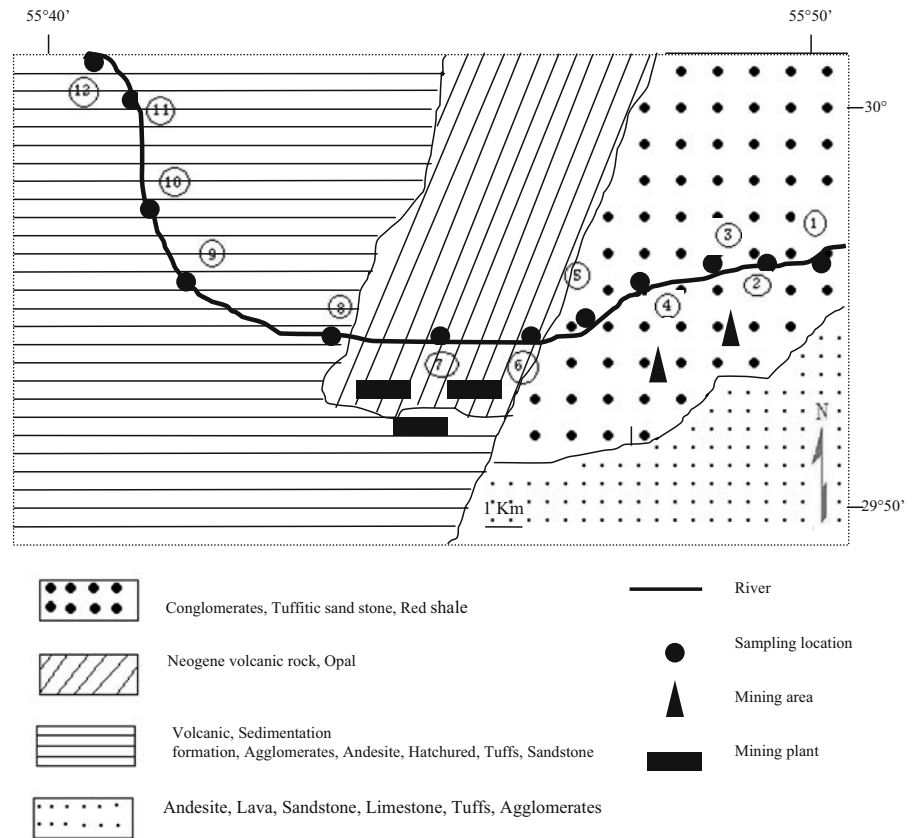
$$I_{\text{geo}} = \text{Log}_2[C_n/(1.5 \times B_n)]$$

Where  $I_{\text{geo}}$  is the geochemical accumulation index,  $C_n$  is the sediment metal concentration and  $B_n$  is the metal concentration in the shale (Gonzalez-Macias et al. 2006, Forstner et al. 1990; Muller 1979). The Enrichment Factor (EF) was computed for metals using:

$$\text{EF} = [(C_n/C_{\text{Al}})_{\text{sample}}]/[(C_n/C_{\text{Al}})_{\text{crust}}]$$

Where  $(C_n/C_{\text{Al}})_{\text{sample}}$  is the ratio of the concentration of the element of concern ( $C_n$ ) to that of Al ( $C_{\text{Al}}$ ) in

**Fig. 1** Map of the study area showing sample sites in Shur River



the sediment sample and ( $C_H/C_{Al}$ ) crust is the same ratio in an unpolluted reference sample (Pekey 2006).

**Results and discussion**

The Shur River flows through three distinct geologic units (Fig. 1). The upper reach of the river, that

includes sampling stations 1–5, encompasses conglomerates, tuff sandstone and red shale. Sampling stations 6 and 7 fall within neogen volcanic rocks and opal. The lower reach of the river, that includes sampling stations 8–12, flows over volcanic sedimentation formations, agglomerates, andesite, tuffs and sandstone. Elemental concentrations (Cu, Pb, Cd, Zn, Fe, Al and Ca), along with organic matter content (LOI), in bed sediment are tabulated in Table 2. The mean concentrations of Cu, Pb, Cd and Zn in Shur River sediments were found to be substantially higher than the mean metal concentrations that are typical of aquatic sediments and crust samples from around the globe (Bowen 1979) (Table 3). Conversely, concentrations of Fe, Al and Ca were considerably lower than the reported, average global concentrations. The lowest sediment metal concentrations were found at stations 1 (upper reach) and 9 through 12 (lower reach). The highest concentrations were found in the middle stations, which are associated with direct mining activities (stations 2 through 4) and ore processing (stations 5 through 7).

**Table 1** Published and obtained data for MESS-1

Element	Published data <sup>a</sup>	Obtained data
Cu	25.1 (3.8)	26.2
Cd	10.8 (1.9)	0.55
Pb	34 (6.1)	32
Zn	191 (17)	187
Fe as Fe <sub>2</sub> O <sub>3</sub>	4.63 (0.25)	4.4
Al as Al <sub>2</sub> O <sub>3</sub>	11.03 (0.38)	10.75
Ca as CaO	0.67 (0.06)	0.66

<sup>a</sup> National Research Council of Canada

Values for trace metals are in mg/Kg and for major elements in % Standard deviations are given within brackets

**Table 2** Concentration of metals in Shur river-bed sediments

Station (no)	Cu	Pb	Cd	Zn	LOI	Fe	Ca	Al
	ppm					%		
1	400	95	2.5	250	2	1.52	1.2	3.56
2	12,000	110	4	780	2.5	2.63	0.45	1.51
3	7,500	120	7	850	2	1.61	0.52	1.31
4	6,000	95	13	750	2.2	2.04	0.6	2.24
5	10,000	230	13	700	2.5	2.17	0.6	0.72
6	9,500	175	7	600	2.2	4.09	0.95	1.78
7	10,500	185	9.5	600	2.5	4.35	0.5	0.78
8	50,000	710	16.5	1,000	3	4.78	1.65	0.86
9	2,500	80	2.5	300	2	1.8	0.9	3.58
10	1,300	45	1.5	300	2	2.55	0.65	2.38
11	135	30	3.5	250	3	2.2	2.54	3.62
12	260	95	2.7	250	2.3	1.53	0.82	4.12
Min	135	30	1.5	250	2	1.51	0.45	0.72
Max	50,000	710	16.5	1,000	3	4.78	2.75	4.12
Mean (present study)	9,174	162	6.85	522	2.35	2.6	1.03	2.2
Mean crust <sup>a</sup>	50	14	0.3	75	–	4.6	4.1	8.2
Mean world sediment <sup>a</sup>	33	19	–	95	–	4.1	6.6	7.2

<sup>a</sup> Bowen 1979

LOI Loss on Ignition

The lowest concentrations of metals in the water column were identified in the upper (station 1) and lower (stations 8 through 10) reaches of river. There was little spatial variation in cadmium concentrations, indicating this is a conservative metal in this aquatic system. Water-sediment interactions that have been reported by many researchers (De 1987; Forstner and Witmann 1981; Helling et al. 1990; Horowitz 1985; Linnik 2001) appear to be distinguished at stations 2 through 7 where sediment concentrations are correlated with water concentrations.

**Table 3** Concentration of metals in Shur river water (ppm)

Station no.	Cu	Fe	Pb	Zn	Cd	Al
1	0.2	1.96	0.12	0.01	0.01	0.36
2	0.03	22.58	0.12	0.65	0.01	0.38
3	0.4	15.68	0.12	0.56	0.03	0.4
4	0.25	15.54	0.14	1.14	0.03	0.36
5	0.37	19.28	0.08	0.76	0.03	0.18
6	2.23	16.22	0.08	2.6	0.03	1.68
7	3.43	6.82	0.16	0.96	0.03	0.68
8	0.01	0.4	0.12	0.03	0.03	0.34
9	0.1	0.9	0.14	0.05	0.03	0.18
10	0.02	0.42	0.08	0.12	0.03	0.1
Min	0.01	0.4	0.08	0.01	0.01	0.1
Max	3.43	22.58	0.16	2.6	0.03	1.68
Mean	0.771	10.98	0.116	0.688	0.026	0.466

In order to quantitatively associate metal concentrations with various sedimentary phases, the sequential chemical partitioning technique was used (Chester and Hughes 1967). The results of the five-step process for heavy metals (Cu, Pb, Cd and Zn) and Fe, Ca and Al, are presented in Tables 4 and 5, respectively. These results were further grouped as a percent of the elements associated with various sedimentary phases:

Loose ions :

Cd(22%) > Zn(20%) > Ca(18.7%) > Fe(11.5%)  
> Cu(9%) > Pb(3%) > Al(1.4%)

Sulfide ions :

Cd(19.7%) > Ca(18.1%) > Zn(15.5%) > Pb(11.85%)  
> Cu(11.5%) > Fe(7%) > Al(2.1%)

Organic ions :

Cd(14.2%) > Cu(13.4%) > Ca(10.2%) > Zn(8%)  
> Pb(3.4%) > Fe(0.5%) > Al(0.16%)

Resistant ions :

Al(96%) > Pb(805%) > Fe(80.2%) > Cu(64.4%)  
> Zn(54%) > Ca(52%) > Cd(42.3%)

With in lattice :

Zn(2.4%) > Cd(1.7%) > Cu(1.7%) > Pb(1.3%)  
> Ca(1.1%) > Fe(0.7%) > Al(0.38)

**Table 4** Chemical partitioning of trace metal in Shur river-bed sediments (ppm)

Station no.	Pb			Cd			Zn			Cu										
	a	b	c	d	e	a	b	c	d	e	a	b	c	d	e					
1	1.7	8	2	83.7	0	0.8	1	2	1	0.08	20	20	2.4	200	7.6	20	50	30	300	0
2	2*	8*	2*	8*	0*	27*	33*	4*	33*	3*	8*	8*	1*	80*	3*	5*	2.5*	7.5*	75*	0*
3	7	17	3.5	80	2.5	0.6	0.4	1	2	0	130	30	210	400	10	1,000	700	1,300	9,000	0
4	6.4*	15.5*	3.2*	72.7*	2.2*	15*	10*	25*	50*	0*	16.7*	3.8*	27*	51.2*	1.3*	8*	6*	11*	75*	0*
5	7	9	4	97.2	2.8	2	1	2	2	0	180	130	200	340	0	800	700	2,000	4,000	0
6	6*	7.5*	3.3*	81*	2.2*	28.5*	14.5*	28.5*	28.5*	0*	21.2*	15.3*	23.5*	40*	0*	10.7*	9.3*	26.7*	53.3*	0*
7	1	3	4	87	0	3	2	3	5	0	220	100	20	400	10	1,000	900	1,000	3,000	100
8	1*	3.1*	4.2*	91.7*	0*	23*	15.5*	23*	38.5*	0*	29.3*	13.3*	2.7*	53.4*	1.3*	16.7*	15*	16.7*	50*	1.6*
9	2.7	3	5.3	220	0	3	2	0.6	7.5	0.1	260	310	10	120	0	2,400	1,800	300	5,500	0
10	1.2*	1.3*	1.5*	95.7*	0.3*	23*	15.3*	4.4*	56.6*	0.7*	37.1*	44.3*	1.4*	17.2*	0*	2.4*	18*	3*	55*	0*
11	5.2	30	2.5	135	2.3	2	2	0.3	3	0	240	220	10	130	0	1,400	1,070	30	7,000	0
12	3*	17*	1.5*	77*	1.5*	27.4*	27.4*	4.2*	41*	0*	40*	36.6*	1.7*	21.7*	0*	14.7*	11.3*	0.3*	73.7*	0*
13	10	40	2.2	130	2.8	3	2	1.5	3	0	200	150	100	130	20	1,900	1,000	600	7,000	0
14	5.4*	21.6*	1.2*	70*	1.8*	31.6*	21*	15.8*	31.6*	0*	33.3*	25*	16.7*	21.7*	3.3*	18*	9.5*	5.7*	66.8*	0*
15	35	56	2	620	0	3	3	0.3	10	0.2	200	200	3.1	600	0	2,700	140	200	47,200	0
16	5*	8*	0*	87	0*	18*	18*	2*	61*	1*	20*	20*	0*	60*	0*	5*	0.2*	0.4*	94.4*	0*
17	0.6	12	6	58.7	3.4	0.6	0.4	0.4	0.7	0.4	50	30	20	200	0	50	550	800	800	300
18	0.7*	15*	7.5*	73.4*	2.7*	24*	16*	16*	28*	16*	16.7*	10*	6.6*	66.7*	0*	2*	22*	32*	32*	12*
19	0.6	8	4	32.4	0	0.3	0.2	0.4	0.6	0	30	12	30	230	0	16	130	500	600	54
20	1.3*	17.7*	9*	72*	0*	20*	13.3*	26.7*	40*	0*	10*	4*	10*	76*	0*	1.2*	10*	38.5*	46.1*	4.2*
21	0.7	7	1.5	20	2.7	0.3	1	0.2	2	0	15	9	6	200	20	3	30	0.1	100	1.9
22	2.3*	23.3*	5*	66.7*	0.8*	8.6*	28.6*	5.7*	57.1*	0*	6*	3.6*	2.4*	80*	8*	2.2*	22.2*	0.2*	74*	1.4*
23	0.6	4	2.5	86.7	1.2	0.5	0.65	0.4	1.15	0	8	7	6.5	200	28.5	1	5	50	200	4
24	0.7*	4.2*	2.7*	91.2*	1.2*	18.5*	24*	15*	42.5*	0*	3.2*	3.2*	2.6*	80*	11.4*	0.4*	2*	19.2*	77*	1.4*
25	0.6	3	1.5	20	0	0.3	0.2	0.2	0.6	0	8	7	3.1	120	0	1	5	0.1	100	0
26	35	56	6	620	3.4	3	3	3	10	0.4	260	310	210	600	28.5	2,700	1,800	2,000	47,200	300
27	Mean	6	16.4	3.3	137.6	1.5	2	1.3	3.2	0.1	129.4	101.5	51.5	262.5	7.8	941	590	568	6,475	38.3

\*Shows percentage of elemental concentration

a: Loosely bonded ions b: Sulfide bonded ions c: Organo-metallic bonded ions d: Resistant bonded ions e: Within lattice bonded ions

**Table 5** Chemical partitioning of major metal in Shur river-bed sediments (ppm)

Station (no)	Fe			Ca			Al								
	a	b	c	d	e	a	b	c	d	e					
1	330	1,300	8	13,500	62	4,000	950	1,250	5,800	0	1	0	3	35,000	596
	2.1*	8.5*	0*	89*	0.4*	33.3*	8*	10.4*	48.3*	0*	0*	0*	0*	98.3*	1.7*
2	9,400	1,900	4	15,000	0	400	600	360	3,000	140	130	700	7	14,260	2
	35.7*	7.3*	0*	57*	0*	9*	13.3*	8*	66.7	3*	1*	4.6*	0*	94.4*	0*
3	6,000	2,100	2	8,000	0	500	1,000	680	3,000	20	560	100	20	12,400	20
	37*	13*	0*	50*	0*	9.7*	19.2*	13*	57.7*	0.4*	4.3*	0.8*	0.1*	94.7*	0.1*
4	3,400	2,800	3	14,000	197	1,400	1,000	700	2,900	0	110	100	20	22,150	20
	16.7*	13.7*	0*	68.6*	1*	23.3*	16.7*	11.7*	48.3*	0*	0.5*	0.4*	0.1*	98.9*	0.1*
5	6,800	3,700	9	11,200	0	1,000	900	500	3,600	0	300	100	10	6,800	0
	31.3*	17*	0*	51.7*	0*	16.7*	15*	8.3*	60*	0*	4*	1.4*	0.1*	94.5*	0*
6	2,000	2,100	5	35,800	995	1,700	2,200	600	5,000	0	80	100	5	17,500	115
	5*	5.1*	0*	87.5*	2.4*	17.9*	23.1*	6.5*	52.5*	0*	0.4*	0.6*	0*	98.4*	0.6*
7	3,400	2,700	4	37,000	396	1,200	900	690	2,000	210	400	600	7	6,700	93
	7.8*	6.2*	0*	85*	1*	24*	18*	13.8*	40*	4.2*	5*	7.7*	0.1*	86*	1.2*
8	500	1,200	3	45,800	297	3,000	6,000	1,700	16,500	300	80	200	2	8,300	18
	1*	2.5*	0*	96*	0.5*	11*	22*	6*	60*	1*	1*	2.3*	0*	96.5*	0.2*
9	50	1,800	630	1,550	20	2,500	2,000	2,000	2,000	0	40	100	180	35,400	80
	0.4*	10*	3.5*	86*	0.1*	27.8*	22.2*	22.2*	22.2*	0*	0.1*	0.3*	0.5*	98.9*	0.2*
10	300	100	600	24,500	0	1,200	800	800	3,300	300	10	800	130	22,800	60
	1.2*	0.4*	2.4*	96*	0*	18.5*	12.2*	12.2*	50.8*	4.5*	0*	3.4*	0.5*	95.8*	0.3*
11	30	100	9	21,500	361	4,000	300	300	17,000	0	30	1,000	20	35,150	0
	0.1*	0.5*	0*	97.8*	1.6*	15.7*	1.3*	1.3*	67*	0*	0*	2.8*	0*	97.2*	0*
12	0.1	0.1	80	15,000	219.8	1,400	700	700	4,100	0	1	500	210	40,450	39
	0*	0*	0.5*	98*	1.5*	17*	8.6	8.6*	50*	0*	0*	1.2*	0.5*	98.2*	0.1*
Min	0.1	0.1	2	1,550	0	400	300	300	2,000	0	1	0	2	6,700	0
Max	9,400	3,700	630	45,800	995	4,000	6,000	2,000	17,000	300	560	1,000	210	40,450	596
Mean	2,684	1,650	113	20,237.5	212.3	1,858	1,446	856.7	5,683.3	79.2	145	358.3	51.2	21,409.2	87

\*Shows percentage of elemental concentration

a: Loosely bonded ions b: Sulfide bonded ions c: Organo-metallic bonded ions d: Resistant bonded ions e: Within lattice bonded ions

**Table 6** Comparison of anthropogenic portion of elements in Shur bed-river sediment

Station	Anthropogenic portion (%)						
	Pb	Cd	Zn	Cu	Fe	Ca	Al
1	12	64	17	25	10.6	51.7	0
2	25.1	50	47.5	25	43	30.3	5.6
3	16.8	71.5	60	46.7	50	41.9	5.2
4	8.3	61.5	45.3	48.4	30.4	51.7	1
5	4	42.7	82.8	45	48.3	40	5.5
6	21.5	59	78.4	16.3	10.1	47.5	1
7	28.2	68.4	75	33.2	14	55.8	12.8
8	12	38	40	5.6	3.5	39	3.3
9	23.2	56	33.3	56	13.9	77.8	0.9
10	28	60	24	49.7	4	49.2	3.9
11	30.6	42.9	12	24.6	0.6	33	2.8
12	7.6	57.5	8.6	21.6	0.6	50	1.7
Min	4	38	8.6	5.6	0.5	30.3	0
Max	30.6	71.5	82.8	56	50	77.8	12.8
Mean	18.1	56	43.7	33.1	19.1	47.3	3.6

Several studies have reported that there can often be a strong association between organic matter and certain elements, particularly cationic metals, such as copper (De 1987; Rosental et al. 1986) In Shur River sediment, however, that relationship appears to be insignificant. Very small amounts of Fe and Mn as sulfide ions can be indicative of a reducing environment (Jha et al. 1990, Jain et al. 2005). In the present study, approximately 7% of the total Fe content was in the form of sulfide ions. Under reducing conditions, mobilization of metals from sediment to overlying water may occur (Karbassi et al. 2001; Saeedi and Karbassi 2006; Karbassi and Aminrnezhad 2004). Further, the sum of loose, sulfide and organic ions are grouped as the anthropogenic portion of

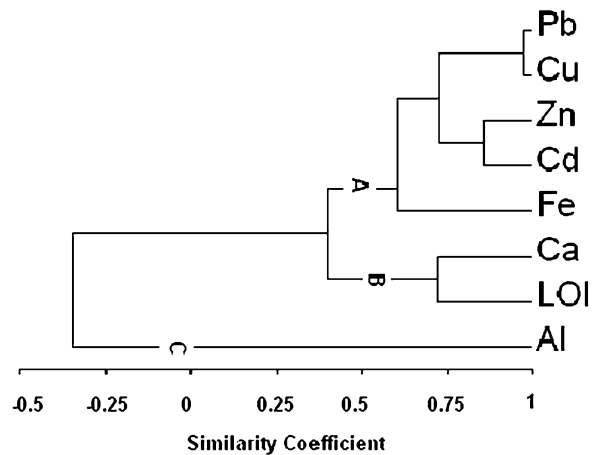
**Table 7** Comparison of various pollution indices in Shur river-bed sediment

Metal	Mean concentration (mg/Kg)	$I_{geo}^a$	$EF^b$	$I_{POLL}^c$
Pb	162	3.78	118.42	0.29
Cd	6.85	0.57	42.7	1.19
Zn	522	4.36	12	0.83
Cu	9174	10.01	264.1	0.49

<sup>a</sup>  $I_{geo} = \text{Log}_2 [C_n / (1.5 \times B_n)]$

<sup>b</sup>  $EF = [(C_n / C_{AI}) \text{ sample}] / [(C_n / C_{AI}) \text{ crust}]$ ; and

<sup>c</sup>  $I_{POLL} = \text{Log}_2 [B_c / L_p]$  - Present study



**Fig. 2** Dendrogram of cluster analysis amongst metals in Shur river bed sediments

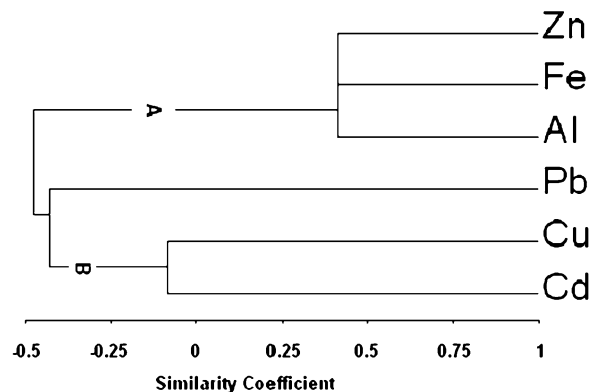
metals (Table 6). In general, the mean anthropogenic portions of the metals examined in this study, as a percent of their mean concentrations, produced the following pattern:

$$Cd(56\%) > Ca(47.3\%) > Zn(43.7\%) > Cu(33.1\%) > Fe(19.1\%) > Pb(18.1\%) > Al(3.6\%)$$

Mean concentrations of metals in Shur River sediments were used to provide a measure of the level of pollution in the study area, based on Muller's index ( $I_{geo}$ ) and the enrichment factor (Table 7). In the present study, Muller's formula was modified as follows:

$$I_{geo} = \text{Log}_2 [C_n / (1.5 \times B_n)] \text{ to } I_{POLL} = \text{Log}_2 [B_c / L_p]$$

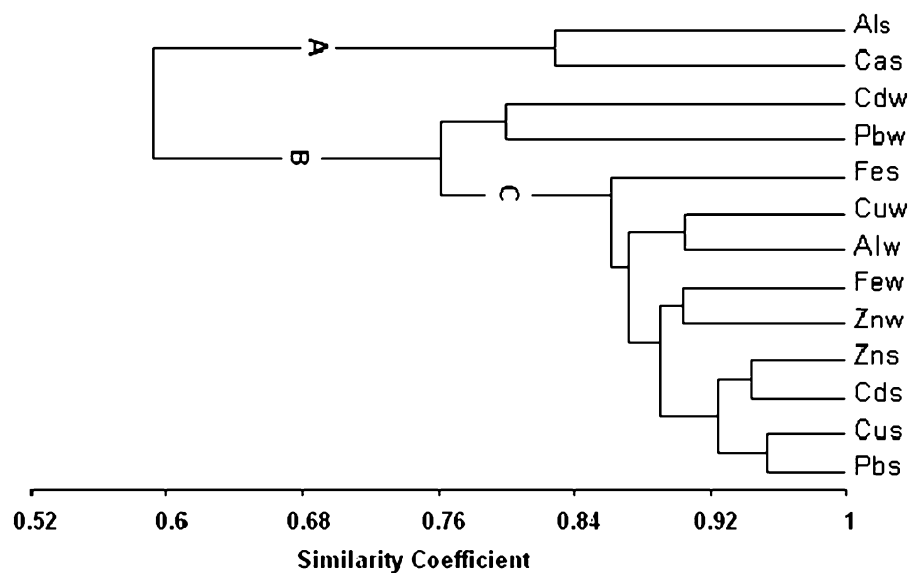
Where  $I_{POLL}$ ,  $B_c$  and  $L_p$  are indicative of pollution intensity, bulk concentration and lithogenous portion,



**Fig. 3** Dendrogram of cluster analysis for dissolved metals in Shur river water



**Fig. 4** Dendrogram of cluster analysis amongst metals in Shur river water and bed sediment



respectively. Muller (1979), as well as other researchers, have used the concentration of metals in shale as a substitute for  $B_n$ , and applied a factor of 1.5 for normalization to background metals concentrations. In the present study,  $B_n$  was computed by subtraction of the anthropogenic portion of metals from bulk concentration or it was obtained through the summation of the 4th and 5th steps of the chemical partitioning study. Since there was not any need in these evaluations to use the shale metal concentrations, the constant factor (1.5) was eliminated. Both EF and  $I_{geo}$  formulae compare present concentrations of metals to their background levels in crust and shale, respectively. In a mineralized area such as the Sarcheshmeh copper mine, where naturally high concentrations of metals are found, such a comparison may lead to erroneous conclusions regarding levels of anthropogenic contamination. For this reason, chemical partitioning results can be substituted for the mean crust and shale levels.

Cluster analysis revealed that Pb, Cu, Zn, Cd and Fe formed cluster “A” (Fig. 2). Lead and Cu demonstrated similar behavior, as did Zn and Cd. Iron joins the Pb, Cu, Zn and Cd cluster, although the similarity coefficient is relatively insignificant. Calcium and organic matter (LOI) formed cluster “B” with a significant similarity coefficient. However, results of chemical partitioning indicate that only 10% of the Ca is present in organic carbonates. Finally, Al forms cluster “C” and joins clusters A and B with a negative similarity coefficient. This strongly suggests that alumina-silicates do not contribute to trace metal

concentrations in the study area. Cluster analysis revealed insignificant relationships among Zn, Cd, Pb, Cu, Fe and Al in Shur River water (Fig. 3). Differences in the metal content of parent rock materials are likely the main reason for the lack of correlation among water-column metals.

Finally, in order to identify water-sediment interactions, the metal concentrations of both media were simultaneously subjected to cluster analysis (Fig. 4). The resulting dendrogram contains three distinct clusters. The high similarity coefficient (0.75) between clusters “B” and “C” indicates that, except for Al and Ca, there is strong relationship between water and sediment metal concentrations in the Shur River. Similar correlations between water and sediment levels have been reported from several global locations (Forstner et al. 1990; Horowitz 1985; Linnik 2001).

## Conclusion

An Environmental Monitoring Planning (EMP) should include reliable and accurate procedures for measuring and interpreting critical environmental data. In the present investigation, the water-sediment interaction was explored empirically through chemical partitioning, as well as statistically through the use of appropriate comparative tests. Partitioning data available in the historical literature were reviewed in order to understand the association of metals with



various sedimentary phases, which were then used to develop new formulae for quantifying the intensity of contamination by chemical stressors. The present study revealed the concentrations of heavy metals in the Shur River sediments were much higher than typical “background” sediment samples and the spatial differences did not appear to be highly correlated with the specific geology and lithology of a sample location, but instead were associated with mining activities. Though metals were found at various concentrations in the anthropogenic fraction, the loosely bonded ions, and thus the most potentially bioavailable, were present at 1.4% to almost 20% of the total metal concentration, indicating that only Cd and Zn might pose an environmental risk. The presence of Ca in loosely bonded ions can be attributed to the nature of Ca to dissociate from contaminant sources at lower pHs. A higher pollution index- $I_{\text{POLL}}$ —was found for Cd and Zn in the study area, while  $I_{\text{geo}}$  and EF failed, to various degrees, to show similar results (particularly for Cd).

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