

Total concentration, speciation and mobility of potentially toxic elements in soils around a mining area in central Iran



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ABSTRACT

The current study was designed to investigate the extent and severity of contamination as well as the fractionation of potentially toxic elements (As, Cd, Cr, Cu, Pb, Zn, Ni) in minesoils and agricultural soils around a Pb–Zn mine in central Iran. For this purpose, 20 agricultural soils and eight minesoils were geochemically characterized. Results showed that minesoils contained elevated concentrations of As (12.9–254 mg kg⁻¹), Cd (1.2–55.1 mg kg⁻¹), Pb (137–6239 mg kg⁻¹) and Zn (516–48,889 mg kg⁻¹). The agricultural soils were also polluted by As (5.5–57.1 mg kg⁻¹), Cd (0.2–8.5 mg kg⁻¹), Pb (22–3451 mg kg⁻¹) and Zn (94–9907 mg kg⁻¹). The highest recorded concentrations for these elements were in soils influenced directly by tailing ponds. Chromium, Cu and Ni content in agricultural soils (with average value of 74.1, 34.6 and 50.7 mg kg⁻¹, respectively) were slightly higher than the minesoils (with average value of 54.5, 33.1 and 43.4 mg kg⁻¹, respectively). Sequential extraction data indicated that there were some differences between the speciation of PTEs in soil samples. In the agricultural soils, Zn and Cd were mainly associated with carbonate bound fraction, As and Pb with reducible fraction, Cu with oxidisable fraction and Cr and Ni with residual phase. With respect to mobility factor values, Zn and Cd in the agricultural soils have been found to be the most mobile while As mobility is negligible. Also, the mobility factor of As, Cd and Pb in agricultural soils adjoining tailing ponds was high. In minesoil sample Cd was most abundant in the carbonate form, whereas other studied elements were mainly present in the reducible and residual fractions; therefore, despite the high total concentrations of As, Pb and Zn in the minesoils, the environmental risk of these elements was low. Based on the obtained data, a portion of Cu, Cr and Ni input was from agricultural activities.

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1. Introduction

Mining activity is considered as one of the most hazardous anthropogenic activities in the world (Acosta et al., 2011) and its disruptive effects on the environment have been known for decades. Generally, mining activities are associated with waste production and the disposal of mine wastes often produces more environmental problems than the mining operations themselves (Fernandez-Caliani et al., 2009). Mining and processing of Pb–Zn ores lead to the production of large amounts of waste rocks and tailings. The disposal of tailings is a major environmental issue that

has become more serious with the increasing exploration for metals and the exploitation of lower grade mineral deposits (Ozkan and Ipekoglu, 2002). The environmental impacts of tailing ponds generally result from their low pH, low organic matter, scarce or nil vegetation and large amounts of potentially toxic elements (PTEs) (Acosta et al., 2011; Favas et al., 2011). PTEs may be transferred from tailing ponds to nearby soils by acid mine drainage and/or atmospheric deposition of wind-blown dust; thus, mine tailings are one of the most important sources of soil pollution (Siegel, 2002; Ferreira da Silva et al., 2004; Boularbah et al., 2006). In recent years, pollution of soil by PTEs in areas adjacent to mine sites has been reported in many countries (Cui and Xin, 2011).

Total concentrations of PTEs provide no information on their likely environmental impacts. Furthermore, the speciation studies could be used to determine the mobility and availability of PTEs. Using the sequential extraction procedure, by which the relative contribution of main soil phases in the retention of different

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elements is determined, it is feasible to predict manner of occurrence, mobility, solubility, bioavailability, toxicity and transport as well as the origin of PTEs (Lasheen and Ammar, 2009; Favas et al., 2011; Nannoni et al., 2011).

Irankuh mining area in central Iran contains 23 million tons of lead–zinc ore (7.4% Pb and 2.4% Zn). With an annual extraction rate of 358,000 tons of ore, this site is one of the major Pb–Zn producers in Iran. Zinc and Pb concentrates are produced by flotation processes. These processes result in the production of considerable volumes of tailings, which are disposed of in large tailing ponds. Agricultural activities in Irankuh area are extensive and the mine's tailing ponds usually neighbor the farms. The main crops are seasonal including vegetables, barley, and wheat. Potatoes and alfalfa are also cultivated. These products are either locally consumed or marketed in Isfahan, a mega city located nearby. Manure is widely used as fertilizer. The farms are mainly irrigated by local ground-water resources. The present study aims to investigate the mobility and bioavailability of PTEs (As, Cr, Cu, Cd, Pb, Zn, Ni) in soils around this mining zone.

1.1. Site description

Irankuh zinc and lead deposits are located along the Irankuh mountain range, 25 km southwest of Isfahan in central west Iran (Fig. 1). The climate of the area is semiarid with annual mean temperature of 14.5 °C. Mean annual precipitation is 140 mm, with rain events falling mostly in autumn and spring. In contrast to little rainfall, the mean evaporation rate in the area is 1705.6 mm year⁻¹. Two

prevailing wind directions are W and SW. Incidence of wind erosion process negatively affects soil in the surrounding areas.

1.2. Geological setting

Geologically, the mine site is located in the Sanandaj–Sirjan structural zone, and is one of the Pb–Zn deposits on the Isfahan–Malayer mineralization belt. The oldest rocks of this area include green-brown to dark grey shales of Jurassic age. These shales are probably the source rocks for Pb–Zn mineralization (Ghazban et al., 1994). Cretaceous carbonate rocks whose thickness is approximately 800 m overly unconformably Jurassic shales. Stratiform lead and zinc mineralization has occurred in folded Cretaceous carbonate sequence. The main ore and gangue minerals in this mineralization zone include sphalerite (ZnS), galena (PbS), pyrite and marcasite (FeS₂), chalcocite (Cu₂S), cerussite (PbCO₃), hemimorphite (Zn₄(Si₂O₇)(OH)₂·H₂O), smithsonite (ZnCO₃), zincite (ZnO), malachite (Cu₂CO₃(OH)₂), hematite (Fe₂O₃), limonite and goethite (Fe₂O₃·H₂O), barite (BaSO₄), gypsum (CaSO₄), dolomite (CaMg(CO₃)) and quartz (SiO₂). Thus, a variety of metals and metalloids (e.g. As, Sb, Cd, Cu) are present as minor elements in the ores.

2. Materials and methods

2.1. Sampling and sample preparation

Fig. 1 displays the location of the sampling points. A total of 28 surface soil samples were collected down to 10–20 cm from zero depth. Twenty samples were collected from soils considered as agricultural soils (contiguous soils). Eight samples

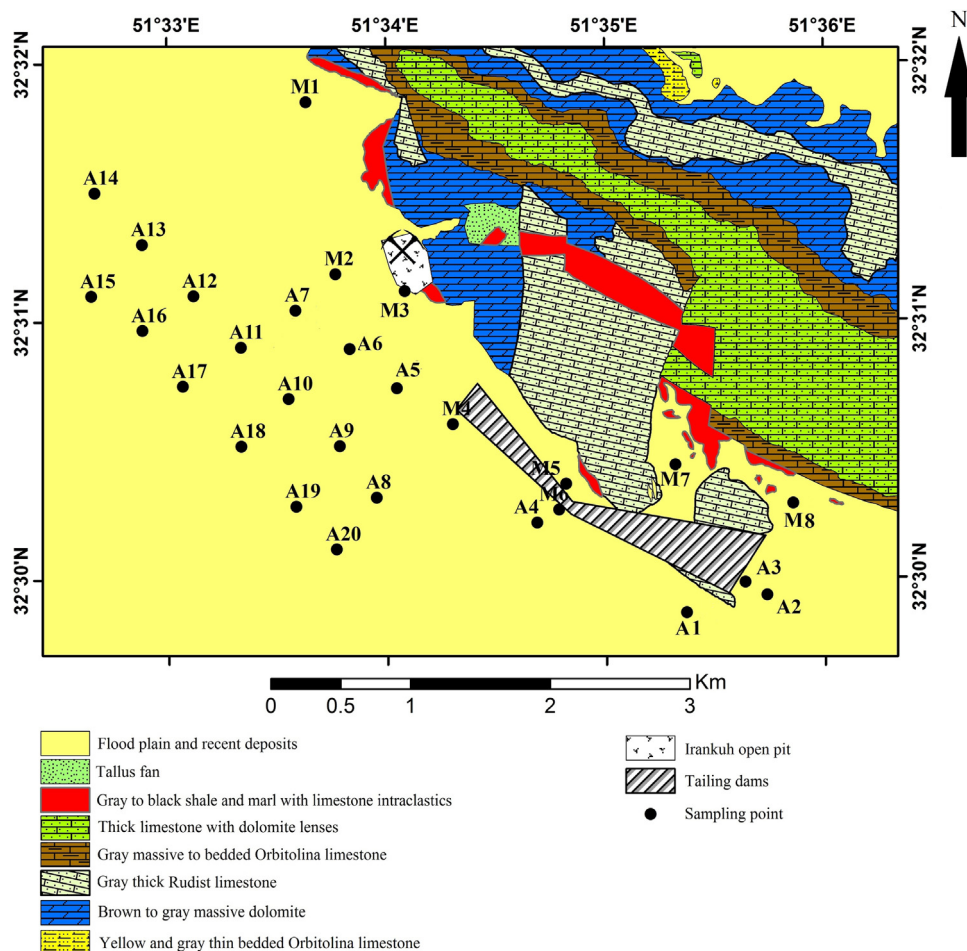


Fig. 1. Geological map of the Irankuh district and location of the sampling sites.

Table 1
General characteristics of agricultural soils, minesoils and tailing samples.

Sampling site	pH	CaCO ₃ (%)	OM (%)	Sand (%)	Silt (%)	Clay (%)	CEC (meq/100 g)
<i>Agricultural soils</i>							
A1	7.9	42	0.8	66	21.3	12.7	12.2
A2	7.7	44.5	0.9	46	25.3	28.7	18.1
A3	7.6	40.5	0.8	46	33.3	20.7	22.2
A4	8.2	48.5	0.3	72	11.3	16.7	15.5
A5	7.6	48.5	0.8	48	27.3	24.7	18.3
A6	7.7	47	0.7	35.3	31.8	32.9	19.6
A7	8.4	43.5	0.6	11.3	33.8	54.9	15.2
A8	7.8	46	1	40.6	39.9	19.5	14.4
A9	7.8	41.5	0.9	34.8	36.8	28.4	18
A10	7.7	45	0.9	21	52.5	26.5	16.1
A11	7.5	47.5	0.9	58.4	16.3	25.3	16.5
A12	7.6	43	0.8	48.2	27	24.8	15.3
A13	7.6	35	0.6	28.5	42.6	28.9	15.4
A14	7.6	40.5	0.8	32.3	39.2	28.5	15.2
A15	7.9	46	0.8	57.2	28	14.8	11.7
A16	7.9	44	0.8	39.2	45	15.8	14.5
A17	8.2	43	0.8	38	40.8	21.2	13.5
A18	8.4	40	0.8	43	38.5	18.5	11.2
A19	8.5	36	0.9	43.7	35	21.3	14.9
A20	8.5	21	0.6	68	14.2	17.8	13
Average	7.9	42.2	0.8	43.9	32	24.1	15.5
Min.	7.5	21	0.3	11.3	11.3	12.7	11.2
Max.	8.5	48.5	1	72	52.5	54.9	22.2
<i>Minesoils</i>							
M1	8	41.5	0.02	32	39.3	28.7	10.9
M2	8.3	44	1.1	65.3	15.8	18.9	16.7
M3	8.4	33.5	0.1	66	21.3	12.7	16.9
M4	8.4	41.5	0.2	58	9.3	32.7	10.2
M5	8.3	45	0.2	43.3	35.8	20.9	13.1
M6	8.5	45.5	0.3	44	37.3	18.7	13.8
M7	8.5	42	0.3	14	61.3	24.7	10.3
M8	8.4	38	0.2	62.2	21.1	16.7	13.6
Average	8.3	41.4	0.3	48.1	30.2	21.8	13.2
Min.	8	33.5	0.02	14	9.3	12.7	10.2
Max.	8.5	45.5	1.1	66	61.3	32.7	16.9
<i>Tailing</i>							
	7.9	42	0.25	26	50.3	23.7	12.8

are representative of minesoils formed either on host rocks (Cretaceous Carbonates) or source units (Jurassic shales). At each sampling site, a composite sample was obtained by mixing and homogenising five subsamples. After drying in laboratory at room temperature, the large fragments and plant residuals were removed and the remaining portion was passed through a 2 mm stainless steel sieve. The sieved samples were ground to about 0.074 mm using an agate mortar and pestle and finally stored in polyethylene bags prior to laboratory analysis.

One representative tailing sample was also collected as composite of sub-samples from 0 to 20 cm depth. The sample was air-dried and subsequently homogenized using an agate mortar and pestle.

2.2. Analysis

2.2.1. Physico-chemical properties

The texture, pH, cation exchange capacity, organic matter and carbonate content of the samples were determined using standard methods. pH was measured in distilled water with a 1:2 solid/solution ratio after equilibration for 15 min (US EPA, 1998, Method 9045D). Hydrometry was used to determine the texture of samples. The organic carbon content of the samples was measured by oxidation with potassium dichromate in a strong acid medium (Chopin and Alloway, 2007). Back-titration method was implemented to measure the carbonate content. The cation exchange capacity was determined by saturation with 1 M ammonium acetate solution, in a buffered medium at pH 7.

2.2.2. Mineralogical composition

In order to investigate the mineralogical composition of the samples, two selective soil samples as well as one tailing sample were analysed by using a Philips PW 1800 XRD.

2.2.3. Total element concentration and sequential extraction analysis

The total concentrations of As, Cr, Cu, Cd, Pb, Zn and Ni were measured after digesting by four acids (HF–HClO₄–HNO₃–HCl) in an open system (Jeffery and Hutchinson, 1983) by ICP-OES (Genesis, Spectro™). The five-stage method of Tessier et al. (1979) was employed for sequential extraction analysis. This method is one of the most thoroughly researched and widely used approaches for evaluation

of possible chemical associations of metals in sediments and soils. Each of the chemical fractions is operationally defined as follows:

Extraction 1: Exchangeable fraction (F_1): 1 g soil (dry wt.) was extracted with 8 ml 1 M MgCl₂, in a 50 ml glass centrifuge tube for 1 h at room temperature with continuous agitation. pH adjusted to 7 using NaOH.

Extraction 2: Weak acid soluble or carbonate-bound fraction (F_2): each residue from exchangeable fraction was extracted with 8 ml of pH 5 (adjusted using HOAc), 1 M NaOAc for 5 h continuous agitation at room temperature.

Extraction 3: Fe/Mn oxide (reducible) fraction (F_3): the residue from the F_2 fraction extracted for 6 h with 20 ml of 0.04 M NH₂OH·HCl in 25% (v/v) HOAc at 96 ± 3 °C with occasional agitation. The pH value was adjusted to 2 using conc. HNO₃.

Extraction 4: Organic matter bound (oxidisable) fraction (F_4):

Step 1: 2 ml 0.02 M HNO₃ and 3 ml 30% H₂O₂ (adjusted to pH 2.0 using conc. HNO₃) were added to the residue from extraction 3. The sample was then placed into the oven and heated at 85 ± 2 °C for 2 h.

Step 2: an additional 3 ml of 30% H₂O₂ at pH 2 was added to the sample and again heated in the oven at 85 ± 2 °C for 3 h, and agitated occasionally.

Step 3: 5 ml of 3.2 M NH₄OAc in 20% (v/v) HOAc was added to the sample and placed into the shaker for 30 min.

Extraction 5: Residual fraction (F_5): the residue from the organic fraction was digested by a HF–HClO₄ mixture.

After each successive extraction, separation was achieved by centrifuging at 4000 rpm for 30 min. The supernatants were separated with a pipette. The residue was washed in 8 ml deionized water and again centrifuged for 30 min. The wash water was decanted. The supernatants were filtered through a 0.45 μm membrane. The solutions were analyzed for As, Cd, Cr, Cu, Ni, Pb and Zn using a Valian 735 ICP-OES. The quality of the sequential extraction procedure was checked by comparing, for each element, the sum of concentrations in five soil fractions with the respective total soil content. The average recoveries of As, Cd, Cr, Cu, Ni, Pb and Zn were 112.1%, 117.1%, 106.1%, 109.3%, 104.8%, 103% and 107.8%, respectively.

2.3. Data analysis

Using SPSS 11.5 software for windows, descriptive data analysis on elements concentrations, pH, CEC, OM and carbonate content of soils was applied. The distribution of the data set was tested for normality by Kolmogorov-Smirnov (K-S) test; when the distribution was not normal (e.g. for As, Cd, Pb and Zn concentration data), the data were log-transformed before statistical treatment. After normalization of the data set, the Pearson correlation analysis was used to determine the relationship between total concentrations of major and trace elements.

To assess the anthropogenic contamination of soil by PTEs and to estimate the enrichment of metal, geoaccumulation index (I_{geo} , Müller, 1969), combined pollution indexes (CPI, Li et al., 2011) and pollution load indexes (PLI, Tomlinson et al., 1980) were all calculated by taking into account the total element concentrations.

3. Results and discussion

3.1. Physico-chemical properties

Table 1 displays the physico-chemical properties of the soil and tailing samples. According to the standard classification of United States Department of Agriculture (USDA, 2003), the agricultural soils are of medium to coarse size, while the minesoils and tailings are medium. The average pH of the agricultural soils and minesoils is 7.9 and 8.3, respectively. The amount of organic matter in agricultural soils ranges from 0.3% to 1%; for minesoils, it falls within the range of 0.02–1.1%. The average cation exchange capacity (CEC) in agricultural soils and minesoils is 15.5 and 13.2 cmol/kg, respectively. Cation exchange capacity depends on the amount of sodium–potassium salts, clays, hydroxides of iron and manganese and the organic matter of samples. The CEC of the soil samples tends to increase with organic matter content ($r^2 = 0.16$) and the percent of the clay fraction ($r^2 = 0.33$) (Fig. 2a). The average carbonate content of agricultural soils and minesoils is 42.2 and 41.4, respectively. The carbonate content of the soil was positively correlated with pH ($r^2 = 0.55$) (Fig. 2b). Given the high carbonate content of the samples, the soils have a high capacity to retain PTEs through adsorption and/or co-precipitation mechanisms. The high carbonate content of the samples is inherited from the parent materials and/or soil amendment with limestone. On the basis of physico-chemical properties of the soils, the agricultural soils and minesoils are Torrifluent and Entisoils, respectively.

The values of the particle size fractions in tailing sample are 26% sand, 50.3% silt, and 23.7% clay; it is therefore classified as silty clay loam. The studied tailing sample has alkaline pH (7.8), low organic matter content (0.25%), high carbonate calcium (42%) and high CEC value (12.1 cmol/kg).

Mineralogical analysis by XRD indicates the presence of dolomite, quartz, muscovite, illite, bassanite, and albite in the tailing sample; the soil samples contain nitratine, orthoclase, calcite, dolomite, quartz, montmorillonite, kaolinite, illite, albite, hollandite and clinocllore (Table 2).

3.2. Element concentrations

The total element concentrations in the soils and tailings from Irankuh area are presented in Table 3. For assessing soil quality, the obtained results were compared with global soil average

Table 2
Minerals identified by XRD analysis of selected soils and tailing samples.

A16	A18	Tailing
Orthoclase	Nitratine	Dolomite
Calcite	Quartz	Quartz
Quartz	Heulandite	Muscovite
Montmorillonite	Albite	Illite
Kaolinite	Clinocllore	Bassanite
Dolomite	Illite	Albite
Illite	Calcite	

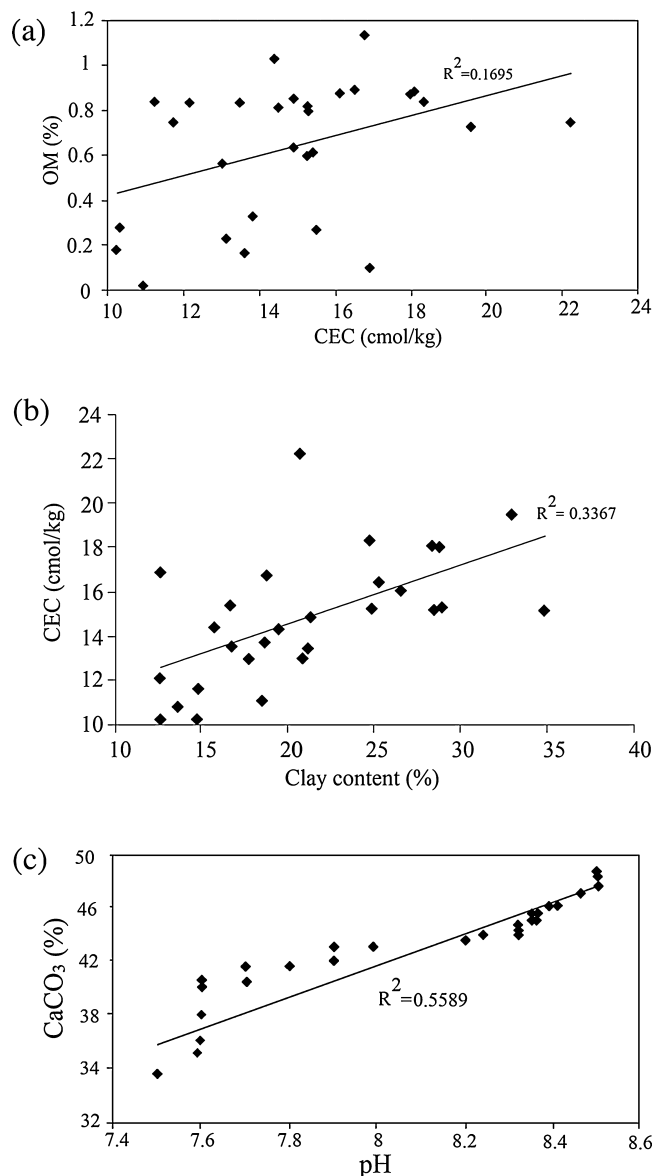


Fig. 2. The relationship between (a) CEC and soil organic matter, (b) CEC and the clay fraction content and (c) carbonate content and pH.

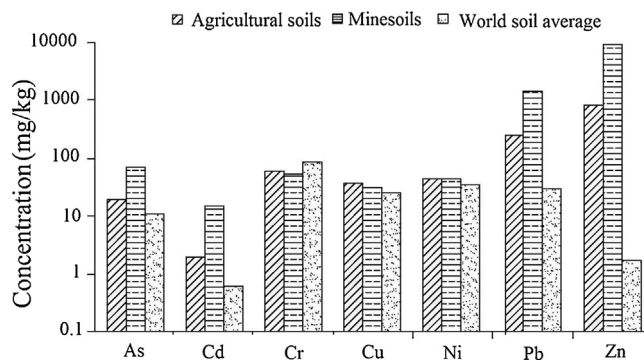


Fig. 3. Mean concentration of elements in the studied soil samples and worldwide uncontaminated soils values (Kabata-Pendias, 2011).

values (Fig. 3). The average concentrations of As, Cd, Pb and Zn in both the minesoils and the agricultural soils exceed the values for global soil average defined by Kabata-Pendias (2011). When compared, the average concentrations of Cr, Cu and Ni are slightly

Table 3
Total element concentration (mg kg⁻¹) in 28 soil samples of the study area.

Sampling site	Al	As	Cd	Cr	Cu	Ni	Pb	Sc	Ti	V	Zn	Zr
<i>Agricultural soils</i>												
A1	32,631	34.2	3.9	62	61	37	284	6.8	1809	56	1173	88
A2	28,154	32.4	4.1	52	35	33	254	5.9	1585	49	1007	77
A3	32,643	19.9	1.7	31	37	32	174	6.5	1753	53	709	81
A4	39,180	17.7	1.2	16	17	29	129	7.5	2122	61	342	94
A5	27,894	13.1	2.1	29	29	32	385	5.7	1622	48	1247	66
A6	29,554	57.1	8.5	35	49	34	3451	6	1595	50	9907	71
A7	34,185	10.3	1.7	47	25	42	210	7.1	1938	59	673	81
A8	71,608	8.8	0.4	103	39	68	33	15.6	3357	107	171	163
A9	62,980	9.7	0.5	109	35	67	41	14.4	3169	97	147	154
A10	55,053	8.1	0.8	97	30	51	77	12.5	2759	78	342	126
A11	63,297	11.8	1.4	87	26	44	181	13.1	2804	76	902	128
A12	64,033	7.3	0.5	104	30	68	39	14.7	3098	101	179	157
A13	63,239	5.5	0.4	86	32	56	31	13.7	3024	87	174	126
A14	67,767	9.9	0.5	90	30	61	29	14.9	3330	99	154	158
A15	60,164	7.8	0.7	96	35	60	39	13.4	2978	89	122	123
A16	70,920	9.3	0.4	100	45	67	43	15.2	3318	100	134	161
A17	65,431	5.6	0.3	79	30	59	41	14.3	3061	93	133	143
A18	63,532	9.5	0.8	104	37	61	28	13.6	2918	90	160	138
A19	59,489	6.6	0.2	75	39	57	23	13.7	2827	86	94	145
A20	60,548	5.5	0.2	79	30	56	22	13.8	2947	86	106	140
<i>Minesoils</i>												
M1	41,707	17.4	1.8	49	24	43	470	8.2	2611	70	1111	105
M2	22,681	254	55.1	55	60	46	6239	4.6	1292	43	26803	62
M3	45,073	64.2	16.4	56	26	36	3953	8.8	2533	72	48899	129
M4	34,990	13	1.2	56	23	45	142	7.2	2201	57	599	105
M5	32,282	61.9	14.5	64	44	42	2039	6.8	1996	57	9446	98
M6	29,411	127.8	31	48	31	48	1177	6	1628	53	6974	84
M7	43,552	12.9	1.4	54	32	46	137	9.1	2791	72	516	113
M8	31,607	21.6	1.4	54	25	41	255	6.6	1803	56	654	84
Average	47628.8	30.8	5.5	68.5	34.1	48.6	711.6	10.2	2459.6	73	4031.4	114.3
Min.	22,681	5.5	0.2	16	17	29	22	4.6	1292	43	94	62
Max.	71,608	254	55.1	109	61	68	6239	15.6	3357	107	48899	163
S.D.	16179.7	51.2	11.8	26.3	10.3	12.3	1473	3.8	649.2	19.5	10361.9	31.9
C.V.	0.3	1.7	2.2	0.4	0.3	0.3	2.1	0.4	0.3	0.3	2.6	0.3
Skewness	0.04	3.6	3.4	-0.1	1.2	0.1	2.8	0.07	-0.3	0.2	3.6	0
Kurtosis	-1.7	14	12.1	-1	1.6	-1.2	7.5	-1.8	-1.5	-1.4	14	-1.3
Global soil average	67,000	11.3	0.6	84	26	34	29	10	5000	105	60	345
Tailing	9984.5	96.1	17.9	7	74	11.5	2835	1.9	544	20.5	6689.5	28

higher in the agricultural soils than in the minesoils, whereas As, Cd, Pb and Zn are more enriched in minesoils (Fig. 3). Also, the distribution of total As, Cd, Pb and Zn concentrations is not normal and follows skewed distributions to higher values (Fig. 4) and their coefficient of variations is greater than 1 (Table 3). However, Cu, Ni and Cr follow distributions closer to normal. Therefore, it can be inferred that the area is probably more contaminated with the elements of the first group, and is less polluted with the second group of elements. In agricultural soils, the highest As, Cd, Pb and Zn concentrations were recorded in soils near the tailing ponds: these soils contain up to 9907 mg kg⁻¹ Zn, 3451 mg kg⁻¹ Pb, 8.5 mg kg⁻¹ Cd and 57.1 mg kg⁻¹ As; thus they are probably transported from tailings to agricultural soils by wind as dust particles. The high concentration of As (96 mg kg⁻¹), Cd (17.9 mg kg⁻¹), Pb (2835 mg kg⁻¹) and Zn (6689.5 mg kg⁻¹) in the tailing sample (Fig. 5) supports this conclusion.

Besides comparisons with the global soil average values, the geoaccumulation index (I_{geo}) of PTEs was also calculated as follows (Müller, 1969):

$$I_{geo} = \log_2[C_n/1.5 B_n]$$

where C_n is the concentration of the examined element 'n' in the soil samples and B_n is the concentration of element 'n' in average shale (Turekian and Wedepohl, 1961). Müller (1969) has identified seven classes of I_{geo} (Table 4). Fig. 6 displays sample percentages in Müller classes for the studied elements. For Cr, Cu and Ni, more

than 50% of the samples fall in unpolluted to moderately polluted class.

The single-factor index (P_i) was calculated as proposed by Li et al. (2011):

$$P_i = \frac{C_i}{C_0}$$

where C_i is the concentration of the element in question in the soil sample and C_0 is the assessment criterion for each element. The average soil composition as reported by Kabata-Pendias (2011) was used as the assessment criterion. There are five levels for P_i (Table 4). Following P_i classification, the soil samples of the Irankuh area can be categorized as follows (Table 5): deficient or clean with Cr, slightly polluted with Cu and Ni, moderately polluted with As and highly polluted with Cd, Pb and Zn. Based on the P_i classification, the magnitude of metal contamination of the Irankuh soil samples yields the following ranking: Zn > Pb > Cd > As > Ni ≥ Cu > Cr. The values of single-factor index for the studied soils are in agreement with geoaccumulation index results.

Abraham and Parker (2008) developed combined pollution index (CPI) as follows:

$$CPI = \frac{\sum_{i=1}^{i=n} P_i}{n}$$

where 'n' is the number of analyzed elements. These researchers defined a classification for CPI (Table 4). CPI values showed that

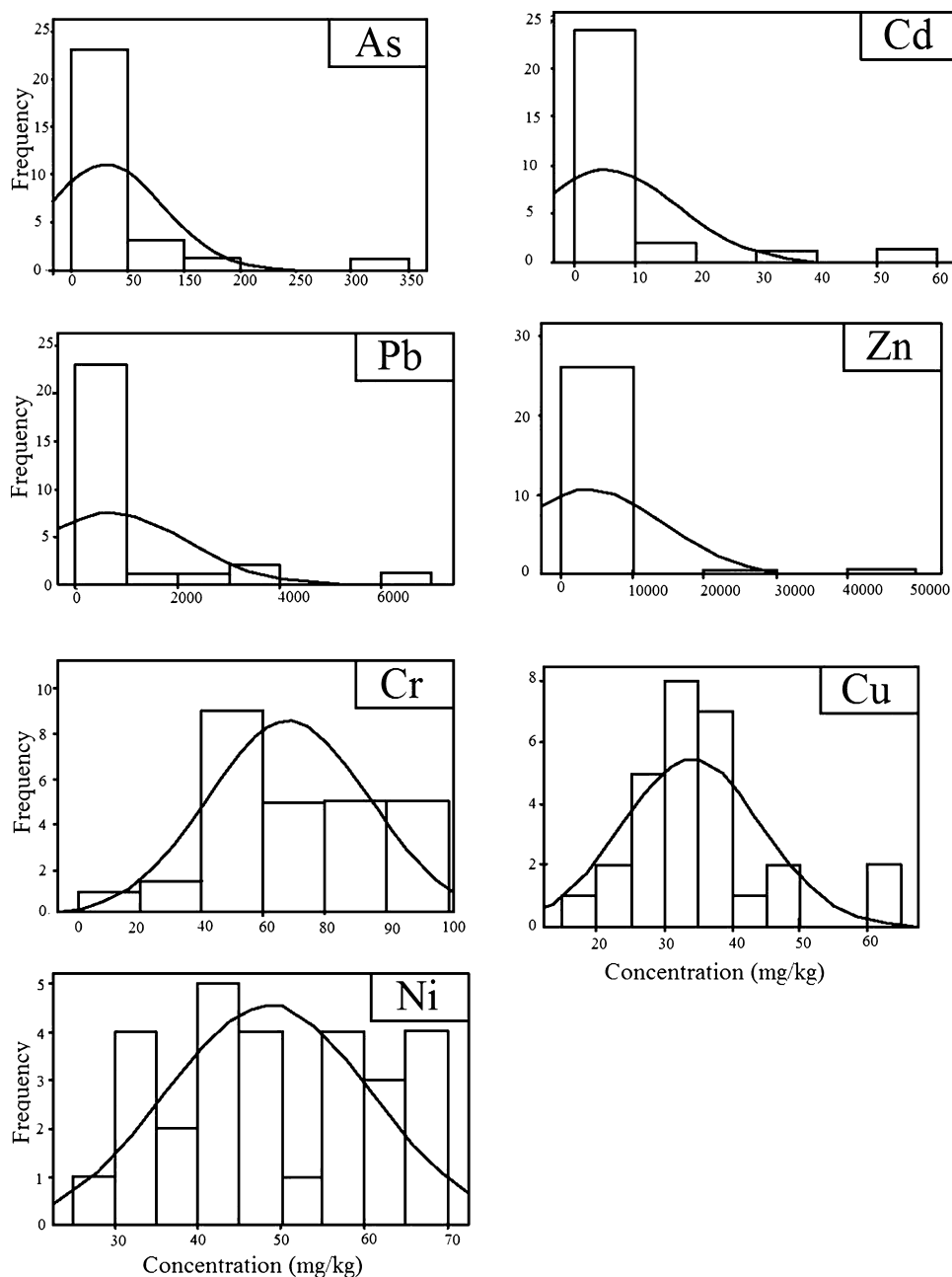


Fig. 4. Frequency distribution of total concentrations of As, Cd, Cr, Cu, Ni, Pb, and Zn in soil samples.

agricultural soils are less polluted than minesoils (Table 5). Also, agricultural soils near the tailing ponds show high CPI values, confirming that the wind transport of particles containing PTEs is the main cause of soil contamination in this area. This is in accordance with general wind directions in the study area.

A quantitative approach of the multi-element contamination can be made based on the pollution load index (PLI) of Tomlinson et al. (1980):

$$PLI = (P_{i1} \times P_{i2} \times P_{i3} \times \dots \times P_{in})^{1/n}.$$

The highest PLI calculated (16.95) is that of an agricultural soil sample around the tailing ponds which shows the impact of tailing ponds on the contamination of agricultural soils.

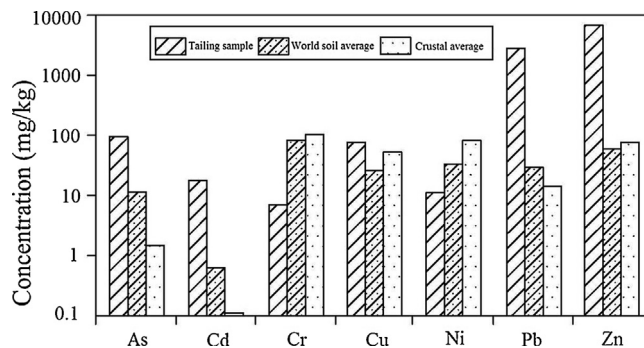
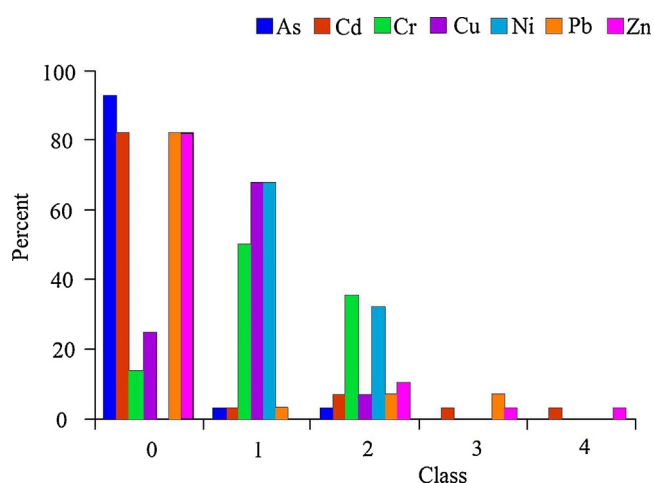


Fig. 5. Concentration of studied elements in the tailing sample compared with worldwide uncontaminated soil values (Kabata-Pendias, 2011) and crustal average values (Taylor and McLennan, 1985).

Table 4
Degree of pollution by PTEs according to I_{geo} , P_i and CPI.

Index	Author	Value	Degree of pollution
I_{geo}	Müller (1969)	$I_{geo} \leq 0$	Unpolluted
		$0 < I_{geo} \leq 1$	Unpolluted to moderately polluted
		$1 < I_{geo} \leq 2$	Moderately polluted
		$2 < I_{geo} \leq 3$	Moderate to strongly polluted
		$3 < I_{geo} \leq 4$	Strongly polluted
		$4 < I_{geo} \leq 5$	Strongly to extremely polluted
P_i	Li et al. (2011)	$I_{geo} > 5$	Extremely polluted
		$C_i < \text{background}$	Excellent
		$P_i < 1$	Clean
		$1 \leq P_i < 2$	Slightly polluted
CPI	Abraham and Parker (2008)	$2 \leq P_i < 3$	Moderately polluted
		$P_i \geq 3$	Heavily polluted
		$CPI \leq 1.5$	Nil to very low
		$1.5 < CPI \leq 2$	Low
		$2 < CPI \leq 4$	Moderate
		$4 < CPI \leq 8$	High
		$8 < CPI \leq 16$	Very high
		$16 < CPI \leq 32$	Extremely high
		$CPI > 32$	Ultra high

**Fig. 6.** Percentage of samples in Müller class, using average shale composition as reference material.

3.3. Speciation of PTEs

Sequential extraction is the best available method to yield information regarding the manner of occurrence, bioavailability, mobilization, transport and source of PTEs (Lasheen and Ammar, 2009). In this study, three samples from agricultural lands (samples A1 and A7 nearby the tailing ponds and sample A17 away from the mine site) and one sample from mine area (Sample M1) were selected. The fractionation of As, Cd, Cu, Cr, Ni, Pb and Zn in four selected soils are given in Fig. 7.

In the studied soils, As was mainly found in the reducible fraction. The next most abundant fraction of As was the residual phase. Exchangeable fraction was the least abundant fraction for As, probably due to the alkaline nature of the samples. In general, As(V) sorption is maximized at acidic pH, and gradually decreases with increasing pH (Arai, 2011). On the other hand, the strong association of As with reducible phases is probably due to the geochemical affinity of this element to Fe–Mn oxides, especially in soils with $\text{pH} > 7$ (Kabata-Pendias, 2011). According to Tessier et al. (1979),

the residual fraction consists of detrital silicates, refractory organic materials and resistant sulfides. Indeed, arsenic usually appears in the form of As^{3+} in sulphide minerals; therefore, the presence of As in residual phase may be due to the isomorphic substitution of As^{3+} in pyrite, marcasite and galena (Kreidie et al., 2011).

Due to the low concentration of Cd in the agricultural soil sample located far from the mine site (Sample A17 with 0.25 mg kg^{-1} total Cd), this element exists only as bound to the reducible and residual phases. The low total concentration of Cd and its presence in reducible and residual fractions indicates that soils far from the mine site are not polluted by this element. Presence of Cd in the oxide phase is due to the neutral to alkaline pH of samples; in soils whose pH is greater than 7.5, iron hydroxides are suitable sites for absorption of Cd (Favas et al., 2011). In samples A1, A7 and M1 with high total content of Cd, this metal exists mainly in the carbonate phase; other studies show that in soils containing elevated Cd levels, precipitates of Cd carbonates (e.g. otavite, CdCO_3) are expected (Anju and Banerjee, 2010; Nannoni et al., 2011). Also substitution of Cd^{2+} for Ca^{2+} in calcite and precipitation of CdCO_3 is expected at high pH (Ghrefat et al., 2012). The mean Cd value in oxidisable fraction of the studied soils was 10.2%. Such small amount is commonly found in soils and sediments, because Cd is not strongly bound to this fraction (Banerjee, 2003). Low solubility of Cd compounds and smaller values of stability coefficients of organic complexes of Cd might be contributing to this issue (Mahanta and Bhattacharyya, 2011).

Chromium was mainly found as residual phase in the studied soils. Similar results have shown that Cr is mainly present in the residual phase of soils, because Cr^{3+} replaces Fe^{3+} and Al^{3+} in silicate minerals, especially clays (Chen et al., 2005). Mineralogical composition of selected soils in the study area points to the presence of Cr in silicate minerals, e.g. clinoclore (Table 2). Based on Fig. 7, in the agricultural soils, the amount of Cr associated with organic matter is higher than in the minesoil. In sludge-amended soils a large fraction of the total Cr can be associated with soil organic matter (Ma and Hooda, 2011).

In agricultural soils, Cu appeared to be associated predominantly with organic fraction, which may be due to extensive application of manure in the study area. The applied manure contains high concentration of Cu (72 mg kg^{-1}). The preferential Cu binding onto organics could be due to both the ease of complexation of Cu(II) with particulate humic and amino acids (Du et al., 2008) and to the greater stability of organic–Cu complexes (Mahanta and Bhattacharyya, 2011). This has been ratified by a number of researchers (e.g. Lasheen and Ammar, 2009). In the minesoil sample, Cu appeared to be associated predominantly with the residual fraction. Other studies also reported that Cu in minesoils is usually associated with residual phase (e.g. Favas et al., 2011). The high proportion of Cu in the residual fraction is likely due to the fact that Cu is chemisorbed on or incorporated in clay minerals; mineralogical data of the studied soils (Table 2) show the presence of clay minerals in the studied soils which confirms this conclusion.

In the studied soils, Pb was predominantly found as reducible fraction; this finding is in agreement with the results of similar studies on mining and smelting areas (Nannoni et al., 2011; Martinez-Martinez et al., 2013). Fe–Mn oxy-hydroxides are important scavengers of metals in soils particularly at $\text{pH} > 7$ (Anju and Banerjee, 2010); in alkaline soils, stable phases such as hematite and goethite may occur (Arias et al., 2008). In agricultural soils located close to the tailing ponds, a high proportion of total Pb was associated with carbonates. This form of lead is mainly in carbonate phases such as cerussite (PbCO_3) and hydro-cerussite [$\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$] which may play an important role in the mobility and bioavailability of this element (Nannoni et al., 2011). CaCO_3 might also act as a strong adsorbent for Pb and could form a complex like $\text{CaCO}_3 \cdot \text{PbCO}_3$ (Anju and Banerjee, 2010).

Table 5
The result of single-factor assessment (P_i), CPI and PLI for tailing and soil samples of the study area.

Sampling site	As		Cd		Cr		Cu		Pb		Zn		Ni		CPI	Class	PLI
	P_i	Class	P_i	Class	P_i	Class	P_i	Class	P_i	Class	P_i	Class	P_i	Class			
<i>Agricultural soils</i>																	
A1	3.03	V	6.5	V	0.74	I	2.35	IV	9.79	V	19.55	V	1.09	III	6.15	High	10.29
A2	2.87	IV	6.83	V	0.62	I	1.35	III	8.76	V	16.78	V	0.97	I	5.45	High	8.27
A3	1.76	III	2.83	IV	0.37	I	1.42	III	6	V	11.82	V	0.94	I	3.59	Moderate	16.95
A4	1.57	III	2	IV	0.19	I	0.65	I	4.45	V	5.70	V	0.85	I	2.20	Moderate	1.89
A5	1.16	III	3.5	V	0.35	I	1.12	III	13.28	V	20.78	V	0.94	I	5.87	High	2.36
A6	5.05	V	14.17	V	0.42	I	1.88	III	119	V	165.12	V	1	III	43.81	Ultra high	7.31
A7	0.91	I	2.83	IV	0.56	I	0.96	I	7.24	V	11.22	V	1.24	III	3.57	Moderate	2.02
A8	0.78	I	0.65	I	1.23	III	1.50	III	1.14	III	2.85	IV	2	IV	1.45	Nil	1.29
A9	0.83	I	0.88	I	1.30	III	1.35	III	1.41	III	2.45	IV	1.97	III	1.46	Nil	1.36
A10	0.72	I	1.35	III	1.15	III	1.15	III	2.66	IV	5.70	V	1.5	III	2.03	Moderate	1.62
A11	1.04	III	2.28	IV	1.04	III	1	III	6.24	V	15.03	V	1.29	III	3.99	Moderate	2.26
A12	0.64	I	0.75	I	1.24	III	1.15	III	1.34	III	2.98	IV	2	IV	1.44	Nil	1.27
A13	0.49	I	0.70	I	1.02	III	1.23	III	1.07	III	2.90	IV	1.65	III	1.29	Nil	1.12
A14	0.88	I	0.83	I	1.07	III	1.15	III	1	III	2.57	IV	1.79	III	1.33	Nil	1.22
A15	0.69	I	1.10	III	1.14	III	1.35	III	1.34	III	2.03	IV	1.76	III	1.35	Nil	1.28
A16	0.83	I	0.72	I	1.19	III	1.73	III	1.48	III	2.23	IV	1.97	III	1.45	Nil	1.35
A17	0.50	I	0.42	I	0.94	I	1.15	III	1.41	III	2.22	IV	1.74	III	1.20	Nil	1.03
A18	0.84	I	1.32	III	1.24	III	1.42	III	0.97	I	2.67	IV	1.79	III	1.46	Nil	1.37
A19	0.58	I	0.25	I	0.89	I	1.50	III	0.79	I	1.57	III	1.68	III	1.04	Nil	0.88
A20	0.49	I	0.30	I	0.94	I	1.15	III	0.76	I	1.77	III	1.65	III	1.01	Nil	0.86
<i>Minesoils</i>																	
M1	1.54	III	3	V	0.58	I	0.92	I	16.21	V	18.52	V	1.26	III	6	High	3.55
M2	22.48	V	91.83	V	0.65	I	2.31	IV	215.14	V	446.72	V	1.35	III	111.5	Ultra high	2.28
M3	5.68	V	27.33	V	0.67	I	1	III	136.31	V	814.98	V	1.06	III	141	Ultra high	2.66
M4	1.15	III	2	IV	0.67	I	0.88	I	4.90	V	9.98	V	1.32	III	2.99	Moderate	8.12
M5	5.48	V	24.17	V	0.76	I	1.69	III	70.31	V	157.43	V	1.24	III	37.3	Extremely high	1.35
M6	11.31	V	51.67	V	0.57	I	1.19	III	40.59	V	116.23	V	1.41	III	31.85	Extremely high	1.97
M7	1.14	III	2.33	IV	0.64	I	1.23	III	4.72	V	8.60	V	1.35	III	2.86	Moderate	3.03
M8	1.91	III	2.33	IV	0.64	I	0.96	I	8.79	V	10.9	V	1.21	III	3.82	Moderate	2.09
<i>Tailing</i>																	
	8.50	V	29.80	V	0.08	I	2.80	IV	96.30	V	111.50	V	0.30	I	35.80	Ultra high	5.60

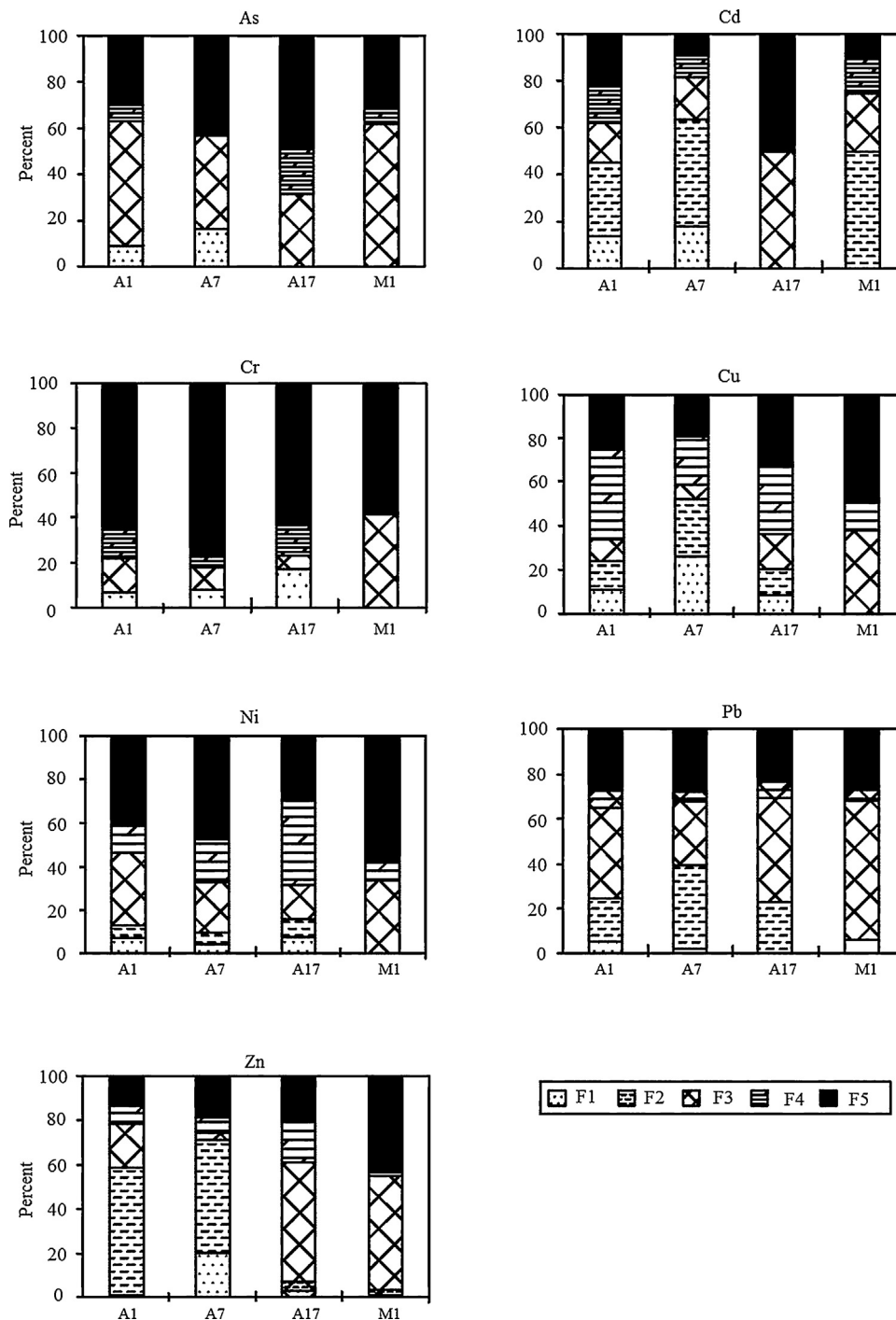


Fig. 7. Speciation of PTEs in soil samples of Irankuh district.

The general fractionation pattern of Zn is similar to Cd in the studied soils, indicating comparable environmental behaviour of the two. In agricultural soils adjacent to the tailing ponds, Zn is mainly associated with carbonate phase, suggesting that calcite (CaCO_3) may act as a strong sink for Zn. In such a case, Zn could exist in the form of complex solid phases such as $\text{CaCO}_3 \cdot \text{ZnCO}_3$ (Martinez-Martinez et al., 2013). Other acid-soluble minerals could be smithsonite (ZnCO_3), sulphates and oxide-sulphates whose presence was detected in the contaminated soils collected in mining and smelting areas (Nannoni et al., 2011). In contrast, reducible Zn was the most dominant fraction in the agricultural soil sample located away from the mine site (Sample A17) and also in

the minesoil (Sample M1). Association of Zn with the reducible phase is due to its tendency to oxy-hydroxides, especially in alkaline conditions (Korfali and Davies, 2004). The high percentage of Zn in the residual phase of minesoil (43%) may be due to the presence of this metal in montmorillonite (Table 2) and resistant sulphide minerals which were not extracted in the previous steps of the sequential extraction analysis (Tessier et al., 1979). Zn did not exceed 10% in the exchangeable fraction in non of the studied samples. This observation is probably due to the alkaline nature of the soil samples, since it is well known that Zn tends to be adsorbed by cation exchange processes in acidic conditions (Favas et al., 2011).

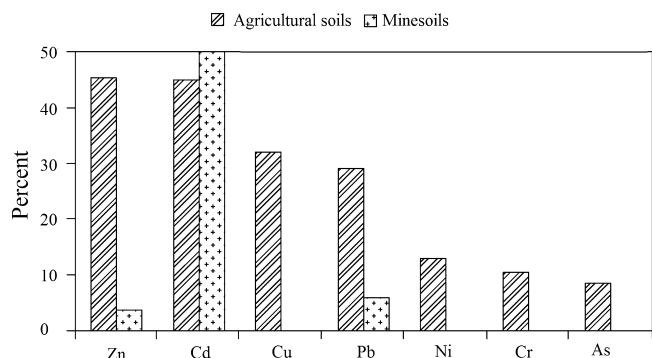


Fig. 8. The PTEs mobility factors defined as the sum of first two fractions divided by the sum of all five fractions (see the text).

Nickel in the studied soils was mainly associated with the residual phase. Other studies have also pointed to the same circumstances in soils in Pb–Zn mining districts (Anju and Banerjee, 2011). The presence of Ni in the residual phase is an indication of its occurrence as inclusions in silicate networks of smectite and illite (Table 2), or its isomorphous substitution with Fe and Al in the spinel group minerals (Favas et al., 2011). A relatively high portion of Ni in the agricultural soils (24.2%) and minesoil (33.9%) was associated with reducible fraction, perhaps due to the alkaline pH of the soils and the siderophile characteristics of this element (Taylor and Kesteron, 2002; Hang et al., 2009). The higher percentage of Ni associated with the oxidisable phase in the agricultural soils, when compared to other samples, demonstrates the impact of agricultural activities on increasing mobility and bioavailability of Ni.

3.4. Mobility of PTEs

The mobility of PTEs in soils generally decreases in the order of extraction sequence (Mahanta and Bhattacharyya, 2011); thus elements in exchangeable (F_1) and carbonate (F_2) fractions are more mobile (Alomary and Belhadj, 2007; Yan et al., 2010). The higher the F_1 and F_2 fractions of a specific metal in the soil, the greater the plant uptake of that metal (Ma and Rao, 1997; Alomary and Belhadj, 2007; Naji et al., 2010; Yan et al., 2010). The relative index of metal mobility was calculated as 'mobility factor' (MF) using the following equation proposed by Kabala and Singh (2001): $MF = \frac{F_1 + F_2}{\sum \text{fractions}} \times 100$

Fig. 8 shows the mobility factor of studied elements. The proportion of mobile to the total sum of fractions for Zn, Cd, Cu and Pb in agricultural soils is appreciably high (the average values for these metals were 45.7%, 45.2%, 32.2% and 29.3%, respectively).

Table 6

Pearson's rank correlation matrix of studied elements in the soil samples.

	Al	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sc	Ti	V	Zn	Zr
Al	1													
As	-.772**	1												
Cd	-.789**	.964**	1											
Cr	.728**	-.433*	-.442*	1										
Cu	-.134	.347	.263	.286	1									
Fe	.261	-.181	-.176	.328	.217	1								
Mn	-.555**	.637**	.612**	-.277	.294	-.220	1							
Ni	.788**	-.517**	-.570**	.879**	.168	.272	-.315	1						
Pb	-.796**	.914**	.945**	-.524**	.197	-.255	.562**	-.649**	1					
Sc	.995**	-.782**	-.804**	.765**	-.095	.289	-.567**	.820**	-.815**	1				
Ti	.972**	-.773**	-.773**	.698**	-.210	.185	-.518**	.765**	-.765**	.963**	1			
V	.982**	-.739**	-.766**	.750**	-.101	.229	-.541**	.840**	-.781**	.982**	.974**	1		
Zn	-.727**	.914**	.950**	-.442**	.204	-.194	.540**	-.595**	.982**	-.748**	-.702**	-.715**	1	
Zr	.959**	-.677**	-.714**	.750**	-.128	.239	-.482**	.799**	-.727**	.957**	.967**	.970**	-.642**	1

* $p < 0.01$.

** $p < 0.05$.

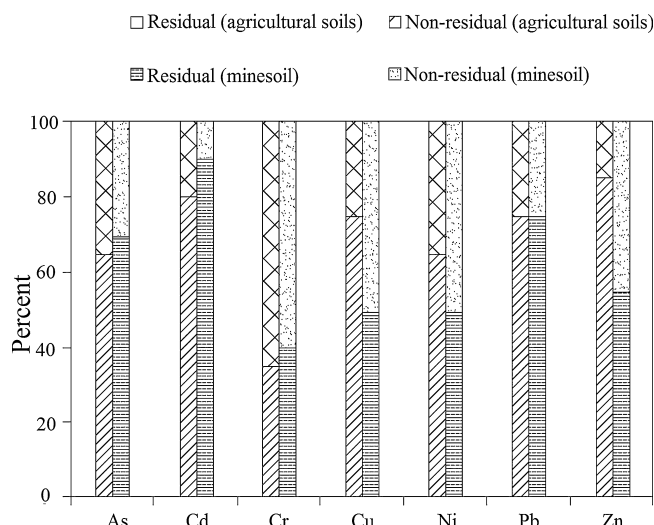


Fig. 9. The percent of PTEs in none-residual and residual phases of studied soils.

Minesoil sample showed a low mobility factor for As (0%), Cu (0%), Ni (0%), Pb (6.2%) and Zn (3.5%). On the basis of the MF values, the order of mobility in studied soils was as Cd (47.6%) > Zn (24.6%) > Pb (17.7%) > Cu (16.1%) > Ni (6.4%) > Cr (5.3%) As (4.3%).

3.5. Source of PTEs

Correctly distinguishing between natural and anthropogenic metal contents in soils is crucial for assessing soil contamination (Desaules, 2012). The sequential extraction data could be used to determine the source of PTEs. This is because the anthropogenically sourced elements preferentially partition to the non-residual phases of the soil, while the residual phase generally reflects background geochemical conditions (Forghani et al., 2009). Inter-element relationships can also provide useful information on the element sources and pathways (Lu and Bai, 2010).

Fig. 9 presents the element concentrations in non-residual and residual phases of the soil samples of the study area. The results indicate that in the agricultural soils, for all the studied elements except Cr, the sum concentrations of the non-residual fractions were significant. Also, in minesoil sample, for all the studied elements except Cr and Ni, the sum contents of the non-residual fractions were considerable. Therefore, in these samples, the anthropogenic sources contributed little to Cr and Ni budget. Inter-element relationships (Table 6) also support this statement. The significant positive correlation between lithogenic elements

and Cr and Ni indicates that these two metals originate from natural sources. On the other hand, significant negative correlation ($p < 0.01$) between As, Cd, Pb and Zn and lithogenic elements (e.g. Al, Sc, Zr, V and Ti) can be interpreted as their introduction to soil through the anthropogenic sources. Significant positive correlations exist between As, Cd, Pb and Zn, confirming their similar geochemical behaviour (e.g. isomorphism of Zn–Cd in wurzite and As–Pb in galena), their similar contamination levels and/or the same input sources such as mining activities (Li and Feng, 2012; Wang et al., 2010).

No significant correlation has been observed between Cu and the rest of the elements, possibly due to a separate source for Cu. Since the average concentration of Cu in agricultural soils was higher than in minesoils (Fig. 3) and the percentage of Cu associated with organic matter fraction of the agricultural soils was relatively high (31.9%), the origin of this element is thought to be agricultural activities. The high concentration of Cu in manure (72 mg kg^{-1}) is in agreement with this viewpoint.

4. Summary and conclusions

This study assessed the total as well as fractional concentrations of As, Cd, Cr, Cu, Pb, Zn and Ni in minesoils and agricultural soils around the Irankuh Pb–Zn mine, located in central Iran. In the area studied, agricultural soils and minesoils contained similar concentrations of Cr, Cu and Ni, while As, Cd, Pb and Zn were present in higher concentration in minesoils.

The concentration of elements studied exceeded the global soil average defined by Kabata-Pendias (2011). The highest concentrations for As, Cd, Pb and Zn were recorded in the soils influenced by the tailing ponds, pointing to the necessity of reclamation programs in the area.

The sequential extraction data revealed different partitioning patterns for the PTEs considered in this study. Also, PTEs speciation showed notable differences in agricultural soils and minesoils. In agricultural soils, Cd and Zn were mainly associated with the carbonate fraction, As and Pb with the reducible fraction, Cu with the organic matter fraction and Cr and Ni with residual fraction. In minesoil sample, major portions of the studied elements, except Cd, were contained in the least mobile fractions (reducible and residual fractions).

The calculated mobility factors indicate that despite high total concentrations of As, Cd, Pb and Zn in the minesoils, the mobility factor suggests potential dangerous situation of only Cd contamination, while the contamination risk of Zn, Cd, Cu and Pb in agricultural soils is considerable and the highest mobility factor of these metals was found in the agricultural soils adjacent to the tailing ponds. The highest mobility factor of Cr was found in the agricultural soil located far from the mining site.

It is widely known that Cu and Zn are essential elements required in trace amounts for plant growth as well as for human and animal health, but in elevated concentrations they are toxic to organism. Arsenic, Pb and Cd are toxic for living organisms even at low concentrations. Therefore, it is recommended to take measures to prevent further transfer of tailing particles into the neighboring agricultural lands.

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