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# Spatial distribution and chemical partitioning of potentially toxic elements in soils around Khatoon-Abad Cu Smelter, SE Iran



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#### ABSTRACT

The objective of this study was to assess the environmental impacts of Khatoon Abad Cu smelter, SE Iran, on soil contamination and to investigate the chemical partitioning of potentially toxic elements (As, Cd, Cu, Mo, Pb and Zn) in the soils. For this purpose, topsoil and subsoil samples were collected and analyzed using standard methods; dust, slag, and concentrate samples were characterized for reference. The results showed elevated concentrations of As (up to 441.8 mg kg<sup>-1</sup>), Cd (up to 11.4 mg kg<sup>-1</sup>), Cu (up to 12,611 mg kg<sup>-1</sup>), Mo (up to 178.2 mg kg<sup>-1</sup>), Pb (up to 316 mg kg<sup>-1</sup>) and Zn (up to 803 mg kg<sup>-1</sup>) in  $< 63 \mu$ m fraction of topsoil samples. The highest recorded concentrations for these elements were in soils collected in downwind direction. The concentration of smelter driven metals in topsoil samples decreased with increasing distance from the Cu smelter and also with increasing depth of the soil samples. The granulometric distribution of the soil samples as well as the mineralogical and geochemical composition of dust sample confirms the impact of smelting activity on the surrounding soils. On the basis of sequential extraction data, the highest percentage for exchangeable, carbonate, reducible, oxidizable, and residual fractions were recorded for Cd (26.5%), Zn (35.5%), As (47.7%), Cu (28.7%) and Mo (37.8%), respectively. The anthropogenic activity (Cu smelting) was the main parameter controlling the metal chemical partitioning because the percentage of non-residual fractions of the studied elements decreased with increasing distance from the Cu smelter and also decreased with increasing depth of the soil samples. Human risk assessment indicated non-carcinogenic (hazard quotient of 1.7) risk to the population and carcinogenic (Incremental Lifetime Cancer Risk of 7.71E-04) risk of As to the children, through the ingestion pathway. The hazard quotient of dermal contact (to the children) is 1.4 for Cu at one site located around the smelter. The results of a single extraction test confirmed the higher risks of As and Cu through ingestion pathway compared with other studied elements. The results of this study show that more attention should be given to the potentially toxic elements (PTEs) pollution in Khatoon Abad area.

#### 1. Introduction

Soil as a main part of the biogeochemical system plays an important role in storage, retention and cycling of elements. The pollution of soils with potentially toxic elements ( $PTE_s$ ) is one of the most important concerns in the mining and smelting districts, unless remediation measures are taken (Shukurov et al., 2014). PTE<sub>s</sub> are critical pollutants, because they are very persistent and the purification of polluted soils via natural processes is very slow. PTE<sub>s</sub> tend to be gradually accumulated in soil and their residence time is very long. For example the residence time is 380, 1000 and 4000 years for Cd, Hg and As, respectively (McLaughlin et al., 1999).

Non-ferrous metals smelting is one of the most important anthropogenic emission sources of metals and metalloids such as As, Sb, Cd, Cr, Cu, Hg, Mo, Ni, Pb and Zn. In the past decades, numerous reports and publications investigate the issue of soil contamination in mining and smelting districts (e.g. Farago et al., 1999; Shih and Lin, 2003; Martley et al., 2004; Bi et al., 2006; Chrastný et al., 2011; Ettler et al., 2011; Kříbek et al., 2014; Zhan et al., 2014; Ettler, 2016). During the smelting processes, these elements are introduced into the environment as volatiles and dust particles (i.e. particulate matters) and are finally deposited on the soil surface especially in the predominant wind direction. PTE<sub>s</sub> associated with particulate matter emitted from smelting operations are usually concentrated in the very fine fraction ( $< 0.5 \mu$ m) which may travel great distances into the environment (Ettler, 2016). The distribution of PTE<sub>s</sub> in soil depends also on other factors such as the soil and particulate mineralogy, the environmental variables (pH, redox conditions, organic matter content, etc.) and the chemistry of smelted

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concentrate and emitted dusts. The respective history of the smelter and the used technology (e.g. the presence/lack of  $SO_x$  gas capture for long time and lack of fugitive gases control) are also important factors for the extent of soil contamination with  $PTE_s$  (Yang et al., 2006). Dissolution of smelter wastes is another important source for soil pollution with PTEs. Kierczak et al. (2013) found that soils in the areas around historic smelters, which were active between the 14th and 16th centuries, are still highly polluted with Cu, Zn, As and Pb, specially due to the centuries-long dissolution of smelter wastes (Ettler, 2016). Smelting sourced PTE<sub>s</sub> eventually may enter the human body through dermal contact, direct ingestion and inhalation of small-size aerosols as well as dusts re-suspended from contaminated soils, which will pose a threat to human health (Bi et al., 2006; Ettler, 2016).

The total content of PTEs in the soil can be a useful criterion indicating contamination intensity; however, the bioavailability, toxicity and mobility of PTEs in the soil are controlled by their chemical partitioning rather than by their total content (Shukurov et al., 2014). Chemical partitioning refers to the binding form of a PTE in the soil solid phase and is influenced by numerous factors (e.g. mineralogy, organic matter content, anthropogenic/natural source of target elements, etc.). In the past decades, more attention has been focusing on the chemical partitioning analysis of trace elements rather than the total metal content (Matong et al., 2016). In order to estimate the metal chemical partitioning in soils and sediments, the sequential extraction procedures (SEPs) with successive extraction steps have been used, although SEP<sub>s</sub> are prone to a variety of limitations (Beckette, 1989). The most important limitations of SEPs include variable experimental conditions, the potential for reagents to be non-selective and for metal ions to re-adsorb to different soil phases, operative definition of different procedures, incomplete dissolution of soil phases, and lack of certified reference materials (Rao et al., 2008; Gunkel et al., 2004; Khedhiri et al., 2011). In all sequential extraction schemes, reactivity of the extractants successively increases and the metal association forms with lesser mobility are decomposed. Because of the "operationally defined" nature of sequential extraction procedures, detailed mineralogical studies are usually necessary in order to investigate the mineralogical speciation of target PTEs in polluted soils (Cohen et al., 1998). In other words, combination of SEPs with mineralogical investigations is extremely useful to predict the actual binding of contaminants in soils.

The Kerman Province, southeast of Iran, is famous for its porphyry Cu-Mo deposits (PCD<sub>s</sub>). Two huge PCD<sub>s</sub>, i.e. Miduk and Sarcheshmeh are the most important Cu mines in Iran. Consequently, smelter plants are established around these PCDs. The Khatoon Abad Cu smelter is situated 180 km to the west of Kerman City, 35 km east of Shahr-e-Babak City, 80 km south of Miduk Cu mine and 45 km NW of Sarcheshmeh Cu complex (Fig. 1). Smelting practices in Khatoon Abad region can result in air and soil pollution. The smelting wastes can be considered as a serious problem in the Khatoon Abad area, because they are disposed around the smelter without proper management strategies. Slag is the most important mineral waste resulting from pyrometallurgy, because it is often rich in toxic elements, in particular Cu, Pb, Zn, As and Sb which can be released into the environment through alteration processes and leaching (Ettler et al., 2009; Ettler, 2016). The Khatoon Abad smelter is located near agricultural farms and pastures. Animal breeding is extensive in this area and the main crop of the region is pistachios.

Due to the probable negative impacts of smelting activities on the surrounding environment, the assessment of the soil contamination levels and identification of potentially hazardous areas around the Khatoon Abad Cu smelter seems to be necessary. On the other hand, the development and implementation of effective soil remediation measures in the Khatoon Abad area needs detailed research on chemical partitioning and bioavailability of  $PTE_s$  in contaminated soils. The main objectives of the present study were: (1) To estimate the total concentrations of PTEs (As, Cd, Cu, Mo, Pb, Zn) in topsoil and subsoil samples, and as reference in concentrate, dust, slag and sludge samples

from the smelter. (2) To assess the health risks of PTEs. (3) To investigate the chemical partitioning of target elements in the soils and evaluate their mobility.

## 2. Climate and geology of the study area

The mean annual temperature and rainfall of the study area are 15.1 °C and 180 mm, respectively; thus, the climate of the area is arid to semiarid. The wind is south and south westerly (Fig. 1) with a speed of 25 m/s (Rastmanesh et al., 2011).

Geologically, the study area is located in the so called Central Iranian Volcano-Plutonic Belt (Berberian and King, 1981). The volcanic and plutonic rocks of this belt are generally associated with porphyry Cu-Mo and skarn mineralization, including deposits such as Sungun, Sarcheshmeh, Miduk and many other sub-economic ore-bodies (Fig. 1). The intrusive suites are characterized by variable age, size and composition, ranging from gabbro to granite (Boomeri et al., 2009). Copper mineralization in the nearby Sarcheshmeh and Miduk mines is associated with granitoid stocks intruded into a thrusted and folded Early Tertiary series comprising andesitic lavas, tuffs, ignimbrites and agglomerates (Shahabpour and Kramers, 1987; Rastmanesh et al., 2011). The Sarcheshmeh ore body contains 450 M tons of ore with average grades of 1.13% Cu and 0.03% Mo (Waterman and Hamilton, 1975). The Miduk ore body contains 170 Mt. at 0.86% Cu and 0.007% Mo (Taghipour et al., 2008). The alteration haloes of adjacent PCD<sub>s</sub> extend up to 1 Km with respect to the granitoid stocks (Boomeri et al., 2009; Shafiei and Shahabpour, 2012).

The surface geology of the study area consists mainly of gravel fans, sand flats, and recent alluvium. Gravel fans are probably the destructive products of the surrounding rock units, i.e. the volcanic suits and ophiolite sequences. The sand flats are the ultimate product of gravel fan's erosion by wind currents. An in situ soil horizon (with maximum thickness of 50 cm) has been developed on gravel fans of the study area. On the basis of soil taxonomy (USDA, 1999), the soils of the study area are mainly classified as Entisols. They are recently formed soils with little or no evidence of pedogenic horizon development in the profile. Entisols are vulnerable to  $PTE_s$  pollution, due to their low organic matter content.

#### 3. Materials and Methods

#### 3.1. Sampling and sample preparation

Twenty four topsoils (0–5 cm) and seven subsoils (10–30 cm) were sampled up to a distance of around 12 km from the Khatoon Abad Cu smelter. In order to investigate the variation of PTE<sub>s</sub> concentration and soil physicochemical parameters with depth, at one location (site S1), sampling was made at three intervals: 0–5, 5–20 and 20–50 cm. Locations of sampling sites were chosen in the downwind (NE direction), upwind (SW direction) and also towards the population centers (W and SE directions). Some locations were also chosen randomly.

Each topsoil sample comprised approximately 1 kg of the five subsamples which were collected using a pre-cleaned stainless-steel spatula and kept in clean PVC bags. In the laboratory, the soil samples were airdried at room temperature and then sieved using a 2 mm stainless-steel sieve. The sieved samples were ground to about 0.074 mm using an agate mortar and pestle and were stored in polyethylene containers until digestion and analysis. In order to investigate the role of silt and clay fraction in metal retention, eleven topsoil samples were also sieved using 63  $\mu$ m stainless-steel sieve. This fraction was used for sequential extraction analysis.

In order to characterize the contamination source, a dust sample from the smelter (sleeved filters before emission to the atmosphere) was analyzed for its mineralogy and  $PTE_s$  concentration. A composite sample was taken from feed ores (concentrates) on shovel of 1 kg every hour for 24 h followed by splitting to 1 kg mass, and analyzed for its



Fig. 1. Location of Khatoon Abad Cu smelter in Central Iranian Volcano-Plutonic Belt and the geological map of the study area. Wind speed and prevalent direction are also shown.

 $\rm PTE_s$  content. Also, the mineralogy and  $\rm PTE_s$  concentration of slag and sludge samples was determined for assessing the environmental impacts of smelting wastes when leached or mixed with soils around the smelter.

For mineralogical studies, samples were air-dried and sieved to < 63  $\mu$ m grain size and then crushed and ground manually using an agate mortar and pestle. In order to separate the < 2  $\mu$ m fraction, the samples were disaggregated with ultrasound and then centrifuged and filtered by membrane 0.45  $\mu$ m filters. Therefore, the < 2  $\mu$ m fraction comprises the fraction < 2  $\mu$ m and > 0.45  $\mu$ m. The clay mineralogy was determined using the oriented preparations, which were submitted to the following treatments: oriented in ambient humidity, ethylene glycol saturated for two days, heated at 375 °C and heated at 550 °C.

# 3.2. Analytical methods

#### 3.2.1. Physicochemical properties of the samples

The < 2 mm fraction was used for the pH, total organic carbon and carbonate content. The pH was determined with 1:1 mixture of dry soil and deionized water (USEPA 1998, Method 9045D). Total organic carbon of the soil samples was measured by  $K_2Cr_2O_7$ -H<sub>2</sub>SO<sub>4</sub> oxidation method (Nelson and Sommers, 1982). The carbonate content was determined by HCl titration method (Jaiswal, 2004).

# 3.2.2. Total concentration of elements in the samples

Total concentration of selected trace elements (As, Cd, Cu, Mo, Pb,

Zn, Sc, Li) was determined using a Genesis SpectroTM ICP-OES instrument after digestion of the samples with HNO<sub>3</sub>/HClO<sub>4</sub>/HF/HCl mixture. The precision of the analyses was checked using duplicate samples, blanks and certified standards (SPEX series). The precision varied from  $\pm$  0.1% to  $\pm$  10% at the 95% confidence level. A repeated check sample was also analyzed by ICP-OES method for quality assurance purposes. The differences between repeated data were close to or < 10% RSD.

Total major element (Al, Fe and Mn) concentrations of concentrate (feeding ore), dust, slag and sludge samples were analyzed using wavelength dispersive X-ray fluorescence spectrometry (Rigaku Primus II with Rh anode X-ray tube). The ground samples were pressed into powder pellets at  $30 \text{ ton cm}^2$ .

### 3.2.3. Single extraction test

In order to evaluate the human bioaccessibility of  $PTE_s$  in the soil samples of the study area, a recently developed single extract method using dilute HNO<sub>3</sub> (ISO-17586:2016, 2016; Rodrigues et al., 2018) was applied. Briefly, 5 g of < 63 µm soil fraction was weighted into a polypropylene bottle and then 50 mL of a 0.43 M HNO<sub>3</sub> solution was added. Bottles were mechanically shaken for 2 h at room temperature. The extraction fluids were filtered through 0.45 µm filters. The concentration of As, Cd, Cu, Mo, Pb and Zn were immediately determined using Genesis Spectro<sup>™</sup> ICP-OES instrument.

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## 3.2.4. Chemical partitioning of PTEs

The chemical partitioning of  $PTE_s$  in selected soil samples was investigated using the Tessier sequential extraction method (Tessier et al. 1979). In each operational fraction step, the extractions were conducted in centrifuge tubes (50 mL with cap). The supernatants were decanted and centrifuged at 4000 rpm for 30 min, filtered through 0.45 µm filters and the residues were washed by deionized water and centrifuged for a further 30 min. The washing was combined with the supernatant of each step. Element concentrations in supernatants were immediately determined using Genesis Spectro<sup>TM</sup> ICP-OES instrument. To evaluate the accuracy of the method, known amounts of the target elements were added to extracts of soil fractions. These additions were within the range of the calibration curve standards. The analyses were repeated in triplicate in order to check the precision of the method. In order to assess the reproducibility of the sequential extraction results in the soil samples, the recovery percentages (R) were also calculated:

$$R = \frac{(C_{f1} + C_{f2} + C_{f3} + C_{f4} + C_{f5})}{C_{total}} \times 100$$

where  $C_{f1}$ ,  $C_{f2}$ ,  $C_{f3}$ ,  $C_{f4}$  and  $C_{f5}$  refer to the metal concentration in exchangeable, carbonate, oxide, organic/sulfide and residual fractions, respectively.

# 3.2.5. Mineralogy and particle size analysis

The crystalline phases of samples was evaluated by X-ray powder diffraction (XRD), using a Bruker D4 diffractometer with Lynxeye detector and operated with Ni-filtered Cu radiation. The mineralogical studies were carried out in two grain size fractions: whole soil (< 63  $\mu$ m) and clay (< 2  $\mu$ m) fractions. The XRD diffractograms were obtained from powders (whole soil samples  $< 63 \,\mu\text{m}$ ) and from oriented (  $< 2 \mu m$ ) in the interval 3 to 70 degrees 20 and 2 to 45 degrees 20, respectively. For whole soil analysis, the samples were homogenized and top filled into a sample holder (Moore and Reynolds, 1997); for the clay fraction, filtered residues were applied to glass objective holder and oriented with spatula movements parallel to the surface to achieve enhanced 00l reflection of phyllosilicates. Proportions of phyllosilicate families registered on the oriented slides were determined following the method proposed by Kahle et al. (2002), to differentiate chlorite and kaolinite the respective (004) and (002) split peak reflections were used (Moore and Reynolds, 1997).

Particle size analyses were carried out by laser diffraction for fine material (particle size <  $150 \,\mu$ m), using a Fritsch Analysette 22 laser diffraction granulometer. Samples were dispersed in deionized water and exposed to ultrasound for 30 s prior to measurement.

## 3.3. Data analysis

# 3.3.1. Geochemical indices

In order to assess the soil contamination around the Khatoon Abad Cu smelter, some geochemical indices including enrichment factor (EF), enrichment index (EI), single factor index ( $P_i$ ) and pollution load index (PLI) were calculated (Table 1). These indices are the most useful criteria for assessing the soil contamination status (Hu et al., 2006; Zhang et al., 2007; Dantu, 2009; Seshan et al., 2010; Candeias et al., 2011; Mmolawa et al., 2011; Kríbek et al., 2010).

# 3.4. Potential health risk assessment

Calculation of the non-carcinogenic and carcinogenic risk for human beings after PTEs exposure helps to the health risk assessment (Ma et al., 2018). Dermal contact, inhalation and ingestion of soil and dust are three major anticipated routes of exposure to potentially toxic elements. The average daily dose (mg kg<sup>-1</sup> day<sup>-1</sup>) of each PTE via ingestion (ADD<sub>ing</sub>), inhalation (ADD<sub>inh</sub>) and dermal contact (Add<sub>derm</sub>) as exposure pathways can be estimated using follow equations (USEPA, 1989):

$$ADD_{ing} = \frac{C \times R_{ing} \times EF \times ED}{BW \times AT} \times 10^{-6}$$
$$ADD_{inh} = \frac{C \times R_{inh} \times EF \times ED}{PEF \times BW \times AT}$$
$$ADD_{derm} = \frac{C \times SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6}$$

The definition and values of these parameters are presented in Table S1. In order to evaluate the potential of chronic (non-carcinogenic) effects of *i*th PTE in the study area, hazard quotient ( $HQ_i$ ) was calculated as follows (USEPA, 1989):

$$HQ_i = \frac{ADD}{RfD_i}$$

where RfD<sub>i</sub> is the Reference Dose (Table S2) at which no adverse effects are expected. If the ADD value is lower than the reference dose (i.e. HQ < 1), there would not be any adverse health effect; otherwise, if the ADD value is higher than the RfD<sub>i</sub> (i.e. HQ > 1), it is likely that the exposure pathway will cause adverse human health effect (USEPA, 1993). To assess the overall potential for chronic effects caused by more than one chemical, the hazard index (HI) was calculated as follows (USEP, 1989):

$$HI = \sum_{i=1}^{n} HQ_i$$

 $\rm HI > 1$  suggests that adverse health effects are likely, whereas  $\rm HI < 1$  points that adverse health effects are unlikely even for sensitive populations (USEPA, 1989). In order to study the non-carcinogenic risk though different routes, the total exposure hazard index was calculated (USEPA, 1989):

$$THI = \sum_{i=1}^{n} HI$$

If THI  $\leq$  1, chronic risks are not probable likely to occur, whereas non-carcinogenic risks are likely to occur when THI > 1 (Zhang et al., 2016).

The USEPA classified arsenic as a group A carcinogen. Therefore, in this study, the carcinogenic risk of arsenic via ingestion, inhalation and dermal contact routes was estimated. In order to assess the carcinogenic risk of arsenic, Incremental Lifetime Cancer Risk (ILCR) was calculated as follows (Cao et al., 2014):

#### $ILCR = ADD \times SF$

SF refers to slope factor of the carcinogenic element. The SF value for arsenic is 1.5 (ingestion), 15.1 (inhalation), and 3.66 (dermal contact) mg kg<sup>-1</sup> day<sup>-1</sup> (IRIS, 2016).  $1 \times 10^{-6} \leq \text{ILCR} < 1 \times 10^{-4}$  is considered as an acceptable level (Ma et al., 2018).

# 4. Results and discussion

# 4.1. Physicochemical properties of the samples

Table 2 presents some physicochemical parameters of the studied soils. According to the standard classification of United States Department of Agriculture (USDA, 2003), the soils were classified as silt loam. The soil samples contain low total organic carbon (between 0.3 and 0.5%), which is perhaps due to their immature characteristics. The pH values are in the range of 8.1–8.9. According to the USDA classification (USDA, 2003), the studied soil samples are moderately to strongly alkaline. The relatively high carbonate content of the soils (2.5–21%) explains the soils pH. It is widely demonstrated that smelting activities result in acidification of surrounding soils due to emission of SO<sub>x</sub> and NO<sub>x</sub> gases (Hu et al., 2006), however, factors such as the high carbonate content of the soils as well as the relatively short time of smelting activity in Khatoon Abad area, have so far prevented potential

#### Table 1

Geochemical indices for contamination assessment of soil samples.

Index	Author	Equation	Value	Degree of pollution
Enrichment factor (EF)	Sutherland (2000)	$\left[\frac{(C / AI)_{sample}}{(C / AI)_{UCC}^*}\right]$	$\text{EF} \leq 2$	Deficiency to low enrichment
			$2\ <\ EF\leq 5$	Moderate enrichment
			$5 \ < \ EF \le 20$	Significant enrichment
			$20\ <\ EF\leq 40$	Very high enrichment
			EF > 40	Extremely enrichment
%Anthropogenic	Eby (2004)	$\frac{\left\{\left(\left[C_{total}\right] - \left(\left[Al_{sample}\right]\left(\frac{\left[C\right]}{\left[AI\right]}\right)_{reference}\right)\right)\right\}}{\left[C_{lotal}\right]} \times 100$	-	-
Enrichment index (EI)	Kríbek et al. (2010)	$EI = \left(\frac{As}{m_{As}} + \frac{Cd}{m_{Cd}} + \frac{Cu}{m_{Cu}} + \frac{Mo}{m_{Mo}} + \frac{Pb}{m_{Pb}} + \frac{Zn}{m_{Zn}}\right)/6$	EI > 1	Seriously affected by anthropogenic activities
P <sub>i</sub>	Li et al. (2011)	$P_i = \frac{C_i}{C_0}$	Pi < 1	Clean
			$1 \le \mathrm{Pi} < 2$	Low level of pollution
			$2 \le Pi < 3$	Moderate level of pollution
			$3 \le Pi < 5$	strong level of pollution
		1.4	Pi≥5	Very strong level of pollution
Pollution load index (PLI)	Tomlinson et al. (1980)	$PLI = (P_{i1} \times P_{i2} \times P_{i3} \times \dots P_{in})^{1/n}$	PLI < 1	unpolluted
			PLI > 1	polluted

\* Upper Continental Crust composition (Taylor and Mc Lenan, 1985).

#### acidification.

# 4.2. Grain size distribution

The granolumetric distribution obtained by laser diffraction in the different samples indicated that the  $< 2 \,\mu$ m fraction may reach up to 30% in the soil samples. The increase in clay size fraction at sites S1, S3, S5, S6 and S11 (located in downwind directions) may be due to accelerated weathering via SO<sub>x</sub> exposure around the smelter. In addition the exposure to SO<sub>x</sub> may affect the micro-texture of soil-aggregates and thus facilitate their disintegration during the brief ultrasound disaggregation (30 s) prior to laser diffraction measurement. The high clay fraction of sampling sites S12 and S27 may be related to the agricultural activity.

On the basis of laser diffraction analysis, the soils of the study area contain 9.8–36.8% and 17.1–73.5% particles having on average a size smaller than 2.5 (PM<sub>2.5</sub>) and 10 µm (PM<sub>10</sub>), respectively (Table 2). These particles (especially PM<sub>2.5</sub>) are dangerous for human health and may cause various respiratory and cardiac diseases (Varshney et al., 2016); therefore, inhalation of soil derived dust particles may be a great risk to the residents of the study area. The < 2.5 and < 10 µm fraction for sludge, dust and concentrate samples may also indicate the serious health problems of these materials for local residents if they are not managed in a closed environment.

# 4.3. Mineralogy of the soils

Fig. 2 presents XRD pattern for a typical whole soil sample (<  $64 \,\mu$ m size fraction) and corresponding oriented clay size diffractogram. On the basis of whole soil mineralogy, soil samples mainly consist of quartz, plagioclase, amphibole, chlorite, illite and calcite confirming the intermediate composition (andesite, dacite and trachyandesite) of gravel fans' parent rocks (i.e. volcanic suits, destructive products of ophiolite sequences, and extensively altered andesitic rocks). Chlorite is present in both whole soil and clay fractions

 Table 2

 Statistical values of physicochemical parameters in the soils of the study area.

(Table 3). Chlorite is considered to be the product of amphibole and pyroxene weathering. This mineral is highly susceptible to acid attacks and is destroyed by exposure to diluted sulphuric acid (Kelm et al. 2014). Chlorite can alter into illite, kaolinite and montmorillonite (Velde, 1985); illite and kaolinite may also be the alteration products of plagioclase (albite, anorthite) and dissolution of K-feldspars in parent rocks by acidic hydrothermal solutions. On the other hand, the presence of smectite in clay size fraction as well as the presence of illite and kaolinite in whole soil fractions is to be expected in hydrothermally imprinted volcanic rocks giving rise to sericitic and argillic alterations. The rocks are found in the superficial gravel fans.

XRD analyses may detect PTEs-bearing phases (e.g. anglesite, plattnerite, galena, quenselite, tennantite, arsenosulvanite and chalcopyrite) in soils near the long term active Cu smelters (Ettler, 2016). However due to the short operation period of the Khatoon Abad Cu smelter, even the most contaminated sector of the study area does not show minerals of which As, Cd, Cu, Mo, Pb and Zn are significant constituent elements above powder XRD limits of detection. Therefore, these elements could be present either as amorphous, poorly crystalline minerals, as impurities, as adsorbed ions on the surface of clay minerals (Chopin and Alloway, 2007) or even as particles of primary sulfides and their oxidation products that are below the level of detection of XRD analysis.

# 4.4. Mineralogy of the dust, sludge and slag samples

Fig. 3 (a, b, c) presents XRD pattern for the dust, slag and sludge samples. The dust sample consists of oxide (hematite, magnetite, spinel), sulfates (hydrated Cu, Zn, and Pb sulfate) and arsenate (Fe arsenate) phases (Fig. 3a). The presence of these phases certainly represents oxidized melt relicts emitted from smelting process and/or the alteration process in dust sample. These minerals could be responsible for the release of  $PTE_s$  into the soils, because they are probably enriched in  $PTE_s$  (for example, arsenate phases are enriched in Pb, Cd and Cu; Ettler et al., 2009). The arsenate and sulfate phases in dust sample are

	рН	Carbonate (%)	Total organic carbon (%)	Clay (%)	Silt (%)	Sand (%)	PM <sub>2.5</sub> (%)	PM <sub>10</sub> (%)
Min.	8.1	2.5	0.4	9.1	61.4	0	9.8	17.1
Max.	8.9	21	0.5	34	80	29.4	36.8	73.5
Average	8.6	8.6	0.3	19.4	68.7	11.9	20.8	39.4



Fig. 2. XRD pattern of a typical soil sample in (a)  $< 63 \,\mu m$  fraction and (b)  $< 2 \,\mu m$  fraction.

#### Table 3

whole mineralogy (<  $63 \,\mu$ m) and phyllosilicate minerals (<  $2 \,\mu$ m) of the soil, slag, sludge and dust samples.

Sample	Minerals
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	Whole mineralogy	Proportion	of phyllos	ilicate mineral	erals (%)	
		Smectite	Mica	Kaolinite	Chlorite	
S1	Quartz, calcite, plagioclase, chlorite, illite, amphibole	6	30	33	31	
S3	Quartz, plagioclase, amphibole, chlorite, illite, calcite	5	29	33	33	
S5	Quartz, calcite, plagioclase, K-feldspar, chlorite, illite, amphibole	5	29	34	32	
S6	Quartz, calcite, plagioclase, chlorite, illite, epidote	7	29	33	31	
S9	Quartz, plagioclase, K-feldspar, chlorite, illite, amphibole	6	27	36	31	
S10	Quartz, plagioclase, chlorite, illite, calcite	10	25	36	29	
S11	Quartz, calcite, plagioclase, K-feldspar, amphibole	6	32	32	30	
S12	Quartz, calcite, plagioclase, K-feldspar, muscovite, chlorite, illite, gypsum	5	34	31	30	
S13	Quartz, calcite, plagioclase, muscovite, K-feldspar, chlorite, amphibole	4	33	32	31	
S15	Quartz, calcite, plagioclase, chlorite, illite, amphibole	n.a.	n.a.	n.a.	n.a.	
S21	Quartz, calcite, cuprite, plagioclase, K-feldspar, chlorite, illite, muscovite	n.a.	n.a.	n.a.	n.a.	
S23	Quartz, plagioclase, amphibole, calcite, chlorite, illite	5	29	34	32	
S25	Quartz, calcite, plagioclase, chlorite, illite, amphibole, hematite	4	33	33	30	
S27	Quartz, calcite, plagioclase, chlorite, illite	n.a.	n.a.	n.a.	n.a.	
S28	Quartz, calcite, plagioclase, amphibole, illite, chlorite, mica	8	34	30	28	
Slag	Fayalite, delafossite	10	28	33	29	
Sludge	Fayalite	n.a.	n.a.	n.a.	n.a.	
Dust	Hematite, spinel phase (including magnetite), copper sulfate hydrate, Fe-arsenate, chalcocyanite, Zn-sulfate (including zincosite), Pb-sulfate (including anglesite), Pb-oxide sulfate	n.a.	n.a.	n.a.	n.a.	

n.a.: not analyzed.

susceptible to hydration and weathering which may result in  $\text{PTE}_{\rm s}$  release into the environment. The chemical composition of the dust sample confirms this conclusion (see below).

The mineralogy of the slag and sludge samples is simple (Fig. 3b, c): slag sample is composed of silicate phase (fayalite), whereas sludge sample is mainly composed of silicate (fayalite) and oxide (delafossite) phases. On the basis of clay fraction mineralogy, there are no phyllosilicates in sludge sample, whereas a trace amount of mica is present in dust and concentrate samples, which may be due to sampling environment or remaining gangue phases for the latter.

# 4.5. Concentrations of elements in the concentrate, dust, slag and sludge samples

The concentrate sample consisted mainly of S (13.1 wt%), Fe (8.9 wt %), Cu (18.5 wt%), SiO<sub>2</sub> (6.5 wt%) and Al<sub>2</sub>O<sub>3</sub> (2.7 wt%). The concentration of PTEs in concentrate sample was very high: As  $(759 \text{ mg kg}^{-1})$ , Cd  $(58 \text{ mg kg}^{-1})$ , Mo  $(1077 \text{ mg kg}^{-1})$ , Pb  $(2681 \text{ mg kg}^{-1})$  and Zn  $(12,751 \text{ mg kg}^{-1})$ , therefore, the smelting of this feed raw material can have significant impact on the environment depending on the element deportment into slag and dust (Larouche, 2001). The chemical composition of dust sample was as follows: Fe (10.9 wt%), Cu (23.2 wt%), S (7.2 wt%), SiO<sub>2</sub> (5.1 wt%), Al<sub>2</sub>O<sub>3</sub> (1.9 wt %), As (94.7 mg kg<sup>-1</sup>), Cd ( $1.9 \text{ mg kg}^{-1}$ ), Mo ( $3893 \text{ mg kg}^{-1}$ ) and Pb  $(727 \text{ mg kg}^{-1})$ . Fig. 4 shows the normalized concentration (with respect to upper continental crust, UCC, composition; Taylor and McLenan, 1985) of target elements in the concentrate and dust samples. The normalized ratio of As, Cd, Cu, Mo, Pb, S and Zn is > 1, indicating the probable effects of these materials on the elements enrichment in soil samples of the study area.

The slag sample was mainly composed of iron oxides (55.4 wt%),  $SiO_2$  (30.1 wt%),  $Al_2O_3$  (5 wt%), and  $K_2O$  (1.5 wt%). The slag sample contained very high concentration of metals and metalloids: As (28,650 mg kg<sup>-1</sup>), Cd (2085 mg kg<sup>-1</sup>), Cu (> 7700 mg kg<sup>-1</sup>), Mo (623 mg kg<sup>-1</sup>), Pb (72,880 mg kg<sup>-1</sup>), S (120,032 mg kg<sup>-1</sup>) and Zn (36,781 mg kg<sup>-1</sup>). In general, the high concentration of S in slag samples indicates that metals dissolved in slag melt are present not only in silicate matrix and pure metallic phases, but can be also associated with S in the form of sulfides (i.e. galena, sphalerite, covellite, etc.) (Ettler et al., 2009). However, as mentioned above, the studied slag sample

contained no XRD detectable sulfide mineral; thus, its high content of  $PTE_s$  points to the concentration of these elements in the structures of fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) and/or in non-crystalline (glass) phases which perhaps contain small inclusions of sulfides. Ettler et al. (2009) showed that the glass phase of slag is a principal carrier of contaminants such as Pb, Zn, Cu, and As. Fayalite may contain trace element and S impurities within the particle structures, because in the reducing atmosphere of smelter furnaces, Fe<sup>2+</sup> can be typically found in this crystallized phase and trace elements of similar ionic radius could enter into the crystal structure of fayalite (Chopin and Alloway, 2007). Fayalite and non-crystalline phases are the most susceptible to weathering and could be responsible for the release of  $PTE_s$  into the nearby soils in the short period of time.

The sludge sample was mainly composed of Fe<sub>2</sub>O<sub>3</sub> (55.4 wt%), SiO<sub>2</sub> (30.1 wt%), Al<sub>2</sub>O<sub>3</sub> (5 wt%), MgO (1.2 wt%) and K<sub>2</sub>O (1 wt%) and contains high concentration of As (377 mg kg<sup>-1</sup>), Cd (90 mg kg<sup>-1</sup>), Cu (204 mg kg<sup>-1</sup>), Mo (80 mg kg<sup>-1</sup>), and S (25,187 mg kg<sup>-1</sup>). With regard to the high concentration of PTE<sub>s</sub> in the waste materials, the potential of this waste to pollute the soils of the study area must be also considered, pending a detailed study on still existing pathways from the smelter to the environment and identification of possible points of intervention.

In comparison, smelting dust is characterized by much lower As, Cd and Pb concentrations compared to the slag sample, suggesting that most part of these elements entered the slag and/or gas-phase because smelting uses heat and chemical reducing agents to decompose the feeding ore, driving off other elements as gases or slag (Gonzalez-Castanedo et al., 2014). Again, the very high concentration of these elements in slag sample and also in the soils collected near the smelter, support this hypothesis.

#### 4.6. Concentrations of elements in the topsoils

The total concentrations of elements for the analyzed samples are presented in Table 4. Generally, the total concentrations of the elements in < 2 mm fraction of the topsoil samples showed an average abundance order of: Cu (92 mg kg<sup>-1</sup>) > Zn (55 mg kg<sup>-1</sup>) > As (23.8 mg kg<sup>-1</sup>) > Pb (13.7 mg kg<sup>-1</sup>) > Mo (1.2 mg kg<sup>-1</sup>) > Cd (0.3 mg kg<sup>-1</sup>). The content of total sulfur in the soils ranged between 110 and 13,243 mg kg<sup>-1</sup> with a mean value of 964.8 mg kg<sup>-1</sup>. Almost 25.8% of the samples had values higher than the maximum







Fig. 4. Normalization diagram for studied elements in concentrate and dust samples. Metal concentrations are normalized to UCC values (Taylor and McLenan, 1985).

concentration  $(1000 \text{ mg kg}^{-1})$  established for non-agricultural surface soils by the Ontario Ministry of Environment (Adamo et al., 2002) which indicates the severe soil contamination with sulfur in some sites. These sites are dominantly located adjacent to the Cu smelter, indicating the effect of sulfur emissions into the atmosphere by smelting processes.

In general, the average total concentration of study  $\text{PTE}_s$  in  $< 63\,\mu\text{m}$  fraction of the topsoils was as follows: Cu  $(2303\,\text{mg}\,\text{kg}^{-1}) > \text{Zn}$   $(210\,\text{mg}\,\text{kg}^{-1}) > \text{As}$   $(84\,\text{mg}\,\text{kg}^{-1}) > \text{Pb}$   $(69\,\text{mg}\,\text{kg}^{-1}) > \text{Mo}$   $(26\,\text{mg}\,\text{kg}^{-1}) > \text{Cd}$   $(2\,\text{mg}\,\text{kg}^{-1})$ . The silt-clay fraction of the soils contains clay minerals which are the common products of silicate weathering. Clay phases such as smectites are characterized by a high cation exchange capacity (80–150 cmol  $\text{kg}^{-1}$  for smectites compared to 10–40 cmol  $\text{kg}^{-1}$  for illites and chlorites, 1–3 cmol  $\text{kg}^{-1}$  for kaolinite) as well as a high specific surface area (Eby, 2004). On the basis of the obtained results (Table 3), > 60% of phyllosilicate minerals of the studied soil samples consist of smectites, mica and chlorite where in particular smectite could adsorb or exchange some of the target

Table 4

Fotal element concentration (mg kg $^{-1}$	) in soil fractions	$(< 2 \mathrm{mm} \mathrm{and} < 63 \mathrm{um})$	. concentrate.	dust. slag	and sludge	samples.

< 2 mm fraction	Al	As	Cd	Cu	Fe	Li	Mn	Мо	Pb	S	Sc	Zn
S1	70,684	24.6	0.3	374	29,442	15	538	1.4	25	489	7.3	78
D1	36,949	12.9	0.2	118	22,710	31	345	1.1	9	211	7	54
S2	68,960	9.3	0.3	109	21,943	12	426	1.5	14	145	5.5	58
S3	67,338	12.3	0.3	83	24,896	14	480	1.1	18	129	6.3	48
S4	66,329	12.3	0.3	66	26,258	17	525	1.3	13	126	7	56
S5	71,447	14.5	0.3	37	35,875	21	641	1	16	125	9.9	64
D5	65,489	12.2	0.3	87	31,531	21	550	1	23	151	9.1	67
S6	65,259	24.6	0.3	323	27,968	13	503	1.5	26	223	6.2	79
S7	73,751	5.9	0.3	52	30,257	14	529	1.3	8	119	6.4	62
S8	75,861	11.4	0.3	40	28,322	11	511	1.4	13	118	6.1	52
S9	79,898	7.8	0.2	40	24,612	14	468	1.3	8	123	5.8	52
S10	83,503	8.4	0.3	32	24,662	12	483	1.2	9	114	6.7	49
D10	85,380	8.8	0.3	79	25,568	15	531	1.2	13	128	7.6	60
S11	62,236	17.8	0.3	371	23,173	14	434	1.2	22	430	5.8	59
S12	50,108	20.8	0.3	53	21,870	32	470	1.3	20	401	6.5	42
S13	50,721	20.6	0.3	54	24,486	36	566	1.4	16	308	8.1	53
D13	49,612	19.5	0.3	35	24,389	37	573	1.1	15	244	7.8	45
S14	30,461	17.2	0.4	202	23,451	27	350	1.4	19	242	6.2	61
\$15	21,241	7.5	0.2	33	17,026	18	268	1	8	110	4.6	36
S16	52,268	25.1	0.2	52	39,905	35	737	1	18	194	13.1	83
D16	52,455 20 524	24.4	0.2	50	38,802	53	739	1	21	104	12.8	// 50
517	30,534	10.0	0.2	30 EE	22,040	50 10	397	1	0	220 142	0.8 E 4	52 47
510 \$10	24,270	7.2 0.7	0.2	53	23,197	19	228	1 2 8	0	143 6087	5.4	47 51
\$19	25,019	5.7 6.7	0.2	33 41	23,197	22	368	2.0	8	174	5.0	JI 40
\$20	20,047	8	0.2	40	25,501	23	346	1	8	170	5.5	45
\$22	33 516	24.1	13	34	14 848	38	329	12	8	13 243	6.4	40
\$23	31,889	17.1	0.2	88	19.926	42	333	1.1	8	1720	6.5	48
\$24	28.224	9	0.2	30	16.868	32	307	1	8	1128	5.8	37
< 63 um fraction	,											
S1	54,900	442	11	12,611	40,052	59	522	56	316	9797	11.6	803
D1	62,232	32	0.5	700	29,111	63	463	2.3	29	629	10.8	111
S5	69,221	15	0.3	148	39,292	35	706	1.13	22	441	13.5	84
\$6	45,382	123	3.4	3183	36,273	55	569	20	99	1338	9.6	314
S9	36,494	14	0.4	199	43,776	47	631	1.22	23	258	9.6	101
S10	37,217	6.7	0.2	47	30,477	26	461	0.85	8	168	10.2	62
S11	49,523	112	3.1	4275	32,946	67	516	178	101	3516	10.2	263
S12	57,927	38	0.5	368	30,064	172	622	2.7	25	687	12	100
S13	63,563	35	0.6	191	31,417	180	755	1.21	19	574	14.9	103
D13	68,290	79	1.7	3114	45,326	33	792	15.1	87	3572	12.9	246
\$16	71,583	27	0.3	499	42,805	34	778	1.43	33	598	13.5	125
Concentrate	11,031	759.1	58	> 15%	> 15%	3	221	1077	2681	224,031	5.4	12,751
Dust	33,844	94.7	2	6530	> 15%	6	374	3893	727	13,623	9.6	8827
Slag	2362	28,651	2085	> 15%	18,994	3	34	623	72,880	120,032	2.6	63,781
Sludge	71,021	499.6	8	4500	50,519	40	2019	106.1	215	25,187	17.1	411
Upper continental crust (Taylor and Mc Lenan, 1985)	80,400	1.5	0.098	25	35,000	20	600	1.5	20	600	11	71
World-soil average (Kabata- Pendias, 2011)	72,000	6.83	0.41	38.9	35,000	21	488	1.1	27	-	11.7	70

USEPA (2015) selected screening levels for residential/industrial soils, respectively (in mg kg<sup>-1</sup>): As (0.67/3.0), Cd (7.0/98), Cu (310/4700), Zn (2300/35,000). CCME (2007) quality guidelines for agricultural/residential/industrial soils, respectively (in mg kg<sup>-1</sup>): As (12/12/12), Cd (1.4/10/22), Cu (63/63/91), Ni (50/50/50), Pb (70/140/600), Zn (200/200/360), Mo (5, 10, 40).



Fig. 5. Comparison of studied elements concentrations in < 2 mm and  $< 63 \mu \text{m}$ fractions of the soil samples.

elements in the  $< 63 \,\mu m$  fraction. However, the competitive effect of Ca and Na for sorption and exchange site positions should be considered. In the  $< 2 \,\text{mm}$  fraction, the average concentration of As exceeds regional screening levels of chemical contaminants proposed by USEPA (2015) and Canadian soil quality guidelines for the protection of the environmental and human health (CCME, 2007) (Table 4). The average Cu content in this fraction exceeds CCME (2007). In the  $< 63 \,\mu m$ fraction, the average concentration of As, Cd, Cu, Zn and Mo exceeded these standard values for different soil land-uses.

On the basis of analytical results, the mean value of total Al, Fe, Mn, Sc and Li concentration is equal in both fractions (Fig. 5) and was comparable with that of the uncontaminated soils (Table 4). In the topsoil samples, these elements showed no significant spatial trend. These observations confirm the natural source of Al, Fe, Mn, Sc and Li. On the other hand, the mean value of total As and Cu concentration in both < 2 mm and  $< 63 \mu \text{m}$  fractions and the mean concentration of Cd, Mo, Pb and Zn in  $< 63 \,\mu m$  fraction was higher than their values in worldwide uncontaminated soils (Kabata-Pendias, 2011). In the topsoil samples, the total concentrations of the PTEs decreased rapidly with increasing distance from the smelter, especially at downwind (NE) direction (Fig. 6a, b, c). Decreased concentrations of contaminants in soils with increasing distance from a point pollution source are a common phenomenon and have been observed at numerous smelter-affected sites (Bi et al., 2006; Ettler et al., 2014). As, Cd, Zn and Pb are known to become easily volatilized in high temperature processes (Shukurov et al., 2014). As the landscape in the studied area is flat, the effect of the topography on the contaminant plume deposition is likely small. The high concentration of PTE<sub>s</sub>, especially As, in the south easterly direction may be due to the impact of Sarcheshmeh Cu smelter (As is transported over greater distances than other elements due to its higher volatility), wind-dispersed particles from mine tailing sites of the Sarcheshmeh Cu complex, and/or agricultural activity. However, in areas where mining and smelting operations are geographically close (e.g. the present site), to distinguish between the sources of pollution, detailed microgeochemical and isotopic investigations are necessary.

# 4.7. Metal concentrations in the subsoils

Fig. 7 shows that the maximum concentrations of As, Cd, Cu, Mo, Pb, S and Zn, in both < 2 mm and  $< 63 \mu \text{m}$  fractions, are mostly found in topsoil layers (0-5 cm). This can be explained by atmospheric deposition resulting from the anthropogenic contamination and/or higher capacity of the soil to immobilize metals at the surface than at depth (Martley et al., 2004). Organic matter can provide a large number of sorption sites, increasing PTEs immobilization by soils. The total organic carbon content of the soils in this study was not significant; on the



Fig. 6. Variation of As, Cd, Cu, Mo, Pb, S and Zn concentrations in different directions and distances from the smelter.

☑ 5-20cm

⊞ 20-50cm



Fig. 7. Element's concentrations in the soil profile.

other hand, it did not show any significant variation with depth; therefore, the anthropogenic emission from Khatoon Abad smelter is the main likely reason for metal enrichment in topsoil layers.

## 4.8. Assessment of soil contamination via different geochemical indices

On the basis of enrichment factor values, the general enrichment of

elements is As (29.5) > Cu (6.1) > Cd (5.6) > Mo (2.2) > Zn (1.4) > Pb (1.1). EF > 1 denotes that the PTE acts like a pollutant (Valente et al., 2015). The percentage contribution of anthropogenic concentration can be calculated from the enrichment factor equation. The anthropogenic percentages for the target elements decreased as follows: As <math>(91.7%) > Cd (75.5%) > Cu (71.3%) > Mo (23%) > Zn (16.2%) > Pb (4.8%). This trend confirms the enrichment of As, Cd and Cu in topsoils mainly from the anthropogenic contributions are found on sites centered on the north east of the smelter.

The extent of anthropogenic contamination of topsoils was expressed using the enrichment index (EI). In the enrichment index equation (Table 1),  $m_{Me}$  is the median value of concentration for the studied element in topsoil. This index actually reflects a higher-than-median or lower-than median average content for the studied elements (Kríbek et al., 2014, 2016). In the study area, sampling sites S1, S6, S11 (adjacent to smelter) and S22 (located in SE direction) have EI > 2.

On the basis of single-factor index ( $P_i$ ) values, the soil samples of the study area can be categorized as follows: heavily polluted with As, Cd and Cu, slightly polluted with Mo and clean with respect to Zn and Pb. Based on the Pi classification, the magnitude of metal contamination of the soil samples yielded the following ranking: As (14.9) > Cu (3.7) > Cd (3) > Mo (1.34) > Zn (0.8) > Pb (0.7). This trend is comparable with EF ranking. These results indicate that the PLI values for the study samples are higher than 1, indicating the pollution of the soils with target elements.

# 4.9. Potential health risk assessment

Table 5 shows results of health risk assessment obtained in this study. The average HQ of inhalation and dermal contact pathways is < 1 for all of the PTEs. The HQ of dermal contact (children) is only higher than 1 for Cu at site 1. The average HQ of ingestion is < 1 for Cu, Cd, Pb, Zn and Mo, (for both children and adults). The average HQ of ingestion is < 1 for As for adults, whereas this value is 1.7 for children. The maximum value of HQ for As through ingestion (for adults) is 2 at

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 Table 6

 Bioaccessible concentration (mg kg<sup>-1</sup>) of PTEs in soil samples.

		00			I	
	As	Cd	Cu	Мо	РЬ	Zn
Min.	0.04	0.01	0.09	0.01	0.01	0
Max.	1.09	0.07	6.29	0.02	0.35	0.17
Average	0.32	0.02	1.31	0.01	0.13	0.06

site 1. The maximum HI value is 24.3 for children and 2.6 for adults at site S1. Therefore, ingestion of soils (for children and adults) and dermal contact (for children) in the study area may pose a non-carcinogenic risk to arsenic and copper, respectively. THI for the study area is s, thus non-carcinogenic risks are likely in the study area.

The bioaccessible content of PTEs in the soils is shown in Table 6. On the basis of average values, the bioaccessibile concentration of the elements may be classified in the following order: Cu  $(1.3 \text{ mg kg}^{-1}) > \text{As}$   $(0.3 \text{ mg kg}^{-1}) > \text{Pb}$   $(0.1 \text{ mg kg}^{-1}) > \text{Zn}$   $(0.05 \text{ mg kg}^{-1}) > \text{Cd}$   $(0.02 \text{ mg kg}^{-1}) > \text{Mo}$   $(0.01 \text{ mg kg}^{-1})$ . Therefore, the results of single extraction test confirmed the results of health risk assessment.

As shown in Table 5, the average ILCR of arsenic for children via ingestion pathway  $(7 \times 10^{-4})$  was higher than acceptable level  $(1 \times 10^{-6} \le \text{ILCR} < 1 \times 10^{-4})$ . Therefore, children living around the Khatoon Abad Cu smelter were exposed to high carcinogenic risks.

#### 4.10. Chemical partitioning of PTEs

Potentially toxic elements are present in soils in different chemical forms with a wide variety of solubilities and bioavailabilities (Li et al., 2015). Chemical partitioning studies of PTE<sub>s</sub> in soil samples provide information about the mobility, bioavailability, and toxicity of target elements. In this study, the chemical partitioning patterns of As, Cd, Cu, Mo, Pb and Zn in <  $63 \,\mu$ m fractions of selected soils around the Khatoon Abad Smelter were investigated. The average recovery values for As, Cd, Cu, Mo, Pb and Zn were 107.4, 105.9, 104.5, 102.2, 109 and 103.9%, respectively, indicating high reliability of data presented in

#### Table 5

Non-carcinogenic (HQ) and carcinogenic (ILCR) health risks to adult and children through different pathways.

		HQ <sub>ing</sub>		HQ <sub>inh</sub>		HQ <sub>dermal</sub>		
		Children	Adult	Children	Adult	Children	Adult	
As	Min.	2.51E - 01	2.69E - 02	7.03E - 06	3.96E - 06	2.26E - 03	1.07E - 04	
	Max.	1.88E + 01	2.02E + 00	9.04E - 04	5.10E - 04	2.91E - 01	1.38E - 02	
	Average	1.71E + 00	1.84E - 01	6.98E - 05	3.94E - 05	2.23E - 02	1.07E - 03	
Cd	Min.	2.68E - 03	2.88E - 04	7.50E - 06	4.23E - 06	1.04E - 03	1.15E - 04	
	Max.	1.46E - 01	1.56E - 02	2.07E - 03	1.17E - 03	6.67E - 01	3.17E - 02	
	Average	1.03E - 02	1.10E - 03	7.89E - 05	4.45E - 05	2.54E - 02	1.21E - 03	
Cu	Min.	9.59E - 03	1.03E - 03	2.68E - 13	1.51E – 13	2.88E - 04	1.37E - 05	
	Max.	4.03E + 00	4.32E - 01	3.34E - 06	1.88E - 06	1.44E + 00	6.83E - 02	
	Average	2.31E - 01	2.47E - 02	8.15E - 08	4.59E - 08	4.31E - 02	2.05E - 03	
Мо	Min.	2.17E - 03	2.33E - 04	6.07E - 08	3.42E - 08	1.03E - 05	9.29E - 07	
	Max.	9.95E + 00	1.07E + 00	2.78E - 04	1.57E - 04	8.96E - 02	4.26E - 03	
	Average	3.31E - 01	3.55E - 02	9.25E - 06	5.22E - 06	2.98E - 03	1.41E - 04	
РЬ	Min.	2.92E - 02	3.13E - 03	8.17E - 13	4.60E - 13	1.70E - 03	8.33E - 05	
	Max.	1.15E + 00	1.24E - 01	2.55E - 06	1.44E - 06	5.88E - 01	2.79E - 02	
	Average	1.09E - 01	1.17E - 02	6.22E - 08	3.51E - 08	2.43E - 02	1.16E - 03	
Zn	Min.	1.53E - 03	1.64E - 04	4.29E - 14	2.42E - 14	4.65E - 05	3.28E - 06	
	Max.	3.42E - 02	3.67E - 03	9.29E - 08	5.24E - 08	2.45E - 02	1.16E - 03	
	Average	4.26E - 03	4.56E - 04	2.27E - 09	1.28E - 09	1.19E - 03	5.66E - 05	
HI		2.40E + 00	2.22E - 01	1.58E - 04	8.92E - 05	1.19E - 01	5.68E - 03	
THI <sub>children</sub>		2.51						
THI <sub>adult</sub>		0.22						
ILCR <sub>ing</sub> (Children)		7.71E - 04						
ILCR <sub>ing</sub> (Adult)		8.26E - 05						
ILCR <sub>inh</sub> (Children)		2.17E - 07						
ILCR <sub>inh</sub> (Adult)		1.22E - 07						
ILCR <sub>dermal</sub> (Children)		1.68E - 05						
ILCR <sub>dermal</sub> (Adult)		8.04E - 07						



this work. The extracted percent values of these elements with respect to their total concentrations are presented in Fig. 8.

## 4.10.1. Exchangeable fraction

The exchangeable fraction, also described as non-specifically adsorbed phase, includes weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interaction and metals that can be released by ion-exchange processes (Rao et al., 2008). Exchangeable elements are the most bioavailable portion of a soil sample and they are released most readily into the environment, especially by changing the environmental conditions such as the soil pH. The results obtained in this study revealed that the exchangeable fraction of As, Cd, Cu, Pb, and Zn accounts for 0-27.1%, 0-35.2%, 0-24.4%, 0-31.9%, and 0-12.5% of the total element content, respectively. Molybdenum was not detected in the first stage of sequential extraction analysis. The absence of exchangeable Mo is probably due to the alkaline pH of the soils. As a whole, oxy-anions of Mo became more soluble, mobile and therefore bioavailable at higher pH values and are retained by soils under acidic conditions, principally on the surfaces of variable-charge minerals, such as the Fe oxides (Chopin and Alloway, 2007).

In comparison with As (with average exchangeable fractions of 8.6%), a relatively higher proportion of exchangeable fraction accounts for Cu (13.1%) and Pb (15.1%). The average percentage of Cd exchangeable fraction was very high (26.5%), resulting perhaps from its adsorption on phyllosilicates (such as illite, smectite, muscovite, chlorite) and amorphous Fe–Mn oxides at alkaline pH conditions. Exchangeable Cd is thought to be readily available for plant uptake.

In general, a decreasing trend of exchangeable fraction of the target elements can be observed with increasing distance from the smelter, especially in the prevailing wind direction; this observation is an indication of the input of these elements from smelting activities in the study area.

#### 4.10.2. Carbonate-bound fraction

Carbonate phases are usually considered as important pools for some elements, especially when organic matter and Fe–Mn oxides of the soil are less abundant. The carbonate bound fraction of elements is a loosely bound and liable to change with environmental conditions, the most important of which is the changes in pH (Kazi et al., 2006; Matong et al., 2016). The results in this study indicated that 0–33.1% As, 0–43% Cd, 0–25.4% Cu, 0–37.5% Pb, and 15.8–46.7% Zn were present as carbonate fraction. Molybdenum was not detected as carbonate phase. The average percentage of carbonate bound As, Cd, Cu, Pb and Zn were 16.2, 30.9, 15.5, 23.3 and 35.5, respectively. The high partitioning of Cd, Pb and Zn with carbonate fraction of the soils was probably due to the similar charge and ionic radius of these metals with Ca (Kabata-Pendias, 2011), which resulted in their ionic substitution. On the other hand, the alkaline conditions of the investigated soils would facilitate the formation of secondary carbonate minerals (e.g. smithsonite) which may explain the fractionation of Cd, Zn and Pb in carbonate phase. Secondary Cd carbonate minerals such as octavite  $(CdCO_3)$  can also exist under such alkaline conditions (pH > 7.6) (Soon, 1981; Yang et al., 2006). On the basis of XRD analysis, the studied elements are probably present in calcite as ion substitution or ultrafine inclusions. Previous studies (e.g. Li et al., 2015; Shukurov et al., 2014) show that relatively high proportions of Cd, Pb and Zn are associated with carbonates in the topsoils around the smelters.

# 4.10.3. Fe-Mn oxide bound fraction

This fraction contains elements bound to iron and manganese oxides and is also considered as a potential mobile phase. Fe-Mn oxides are well known 'sinks' in the surface environment for PTEs and are thermodynamically unstable under the anoxic circumstances (Anju and Banerjee, 2010). The results obtained in this study revealed that the reducible fraction of As, Cd, Cu, Mo, Pb, and Zn accounted for 22.1-71.4%, 0-10%, 1.3-21.8%, 0-50%, 16-48.6%, and 4.5-38.3% of the total element content, respectively. On average, 47.7, 1.2, 10.29, 36.8, 34 and 14% of total As, Cd, Cu, Mo, Pb and Zn are present as oxide-bound fraction, respectively. The strong partitioning of As, Pb and Mo with oxide fraction is mainly due to their high affinity for the amorphous iron and manganese hydrous oxides (Ramos et al., 1994; Shukurov et al., 2014), particularly at high pH ranges (pH > 7) (Li and Thornton, 2001). It may also be an indication of anthropogenic source for these elements (Adamo et al., 2002; Popescu et al., 2013, Li et al., 2015). Zemberyova et al. (2010) found that the largest proportion of Mo in the unpolluted soils was exclusively in the residual fraction and its release was unlikely under environmental conditions. However, in the studied soil samples a high proportion of this element was associated with reducible fraction. This observation suggests that new anthropogenic binding phases of Mo have probably been formed in the study area. The high proportion of Pb (34%) in the oxide fraction can also be explained by the low total organic carbon content of the studied soils; in soils with low total organic carbon content, Pb is commonly associated with oxide fraction (Kabata-Pendias, 2011).

# 4.10.4. Organic-sulfide bound fraction

This fraction would be released into the environment if conditions became oxidative (Anju and Banerjee, 2010). The results here indicated that 0-38.5% As, 0-80% Cd, 15.4-58.9% Cu, 0-63.3% Mo, 0-44% Pb, and 8.6-39% Zn were present as the organic-sulfide bound fraction. The average values of As, Cd, Cu, Mo, Pb and Zn oxidizable fraction were 15.4, 11.9, 28.7, 25.4, 15.6 and 25.8%, respectively. The Tessier sequential extraction scheme is not able to distinguish between associations with organic matter and sulfides (Anju and Banerjee, 2010). On the other hand, the organic matter content of the soils was very low (0.3-0.5%), thus the metals extracted in this fraction should owe their origin to metal sulfides. As, Cu, Mo, Pb and Zn are chalcophile elements commonly occur in PCD mineralization zones; these elements are present as main elements or ionic substitution in molybdenite, galena, sphalerite, chalcopyrite and pyrite. These results were consistent with the strong ability of combining with sulfides for Cu, Mo, Pb and Zn ions in soils (Motong et al., 2016).

#### 4.10.5. Residual fraction

This fraction of elements must be present either in silicate minerals of which they are constituent parts, or as impurities in the crystal structure of other silicate minerals (Chopin and Alloway, 2007). The residual fraction of elements has the lowest mobility and bioavailability and comes mainly from natural sources (Panichayapichet et al., 2008; Devesa-Rey et al., 2010; Li et al., 2015). All target elements are associated with the residual phase: this fraction accounted for 6.5–43.8, 20–100, 12.6–69.7, 31.4–100, 5.6–31.6 and 5.9–44.8% of total As, Cd, Cu, Mo, Pb and Zn, respectively (on average, 12% As, 29.5% Cd, 32.5% Cu, 37.8% Mo, 12% Pb and 16.3% Zn). The relatively high percentage of Mo in residual phase of the studied soils may be due to the presence



Fig. 9. Percent of studied elements in none-residual and residual phases of soil profile.

of ultrafine Mo phases, locked minerals enclosed in micro-aggregate or minerals that were not broken up by any sample milling, and/or substitution of Fe<sup>3+</sup>, Ti<sup>4+</sup>, Al<sup>3+</sup> and Si<sup>4+</sup> by Mo in feldspars, ferromagnesium minerals (biotite, amphibole, pyroxene) and smectites.

The presence of Cu and Pb in residual fraction may be interpreted by their relatively high content in andesite as the main soil parent material, due to the tendency of these two metals for accumulating in intermediate to felsic rocks. The binding of Pb as residual fraction may also be explained in part by the existence of stable mineral phases such as pyromorphite and/or anglesite (Yang et al., 2006), however, such minerals remain below the limit of detection of powder XRD for whole soil and  $< 2 \,\mu$ m fractions. The residual Zn and As could be present at phyllosilicates, or as ultrafine locked ore phase. A definition of this hypothesis will require micro-chemical analysis.

The association of metals with residual fractions of topsoils increases with distance from the Cu smelter. Again, this observation indicates that the accumulation of studied elements in topsoils of the study area is partly due to the deposition of atmospheric emissions from the Khatoon Abad Cu smelter.

#### 4.10.6. Chemical partitioning of the studied PTE<sub>s</sub> in soil profile

The variation of the element partitioning in soil profile could provide information about their recent anthropogenic enrichment, if the concentrations of the elements associated with the more mobile fractions (F1–F4) are higher at the surface than at the bottom of the soil profile (Forghani et al., 2009). Fig. 9 shows that there were obvious differences in element partitioning with depth in soil profile collected at S1 site. For all the elements in this study, the sum concentrations of the non-residual fractions were higher in topsoils. It points to the fact that the elements are mainly from an anthropogenic source (ore smelting). On the basis of PTEs chemical partitioning pattern in soil profile, it may be concluded that the PTE<sub>s</sub> are expected to be released from the soil solution over a reasonable time span under the conditions normally encountered in nature (Tessier et al., 1979).

# 5. Summary and conclusions

This study investigates the mineralogical and geochemical composition of the soils around the Khatoon Abad Cu Smelter, SE Iran. On the basis of analytical results, the soils of the study area are the weathering products of volcanic rocks of the region. These soils contain high concentrations of As and Cu in both  $< 63 \,\mu\text{m}$  and  $< 2 \,\text{mm}$  fractions in comparison with worldwide uncontaminated soils, whereas Cd, Mo, Pb and Zn concentrations in  $< 63 \,\mu\text{m}$  are higher than their values in uncontaminated soils. On the basis of results in this study, the highest concentrations for As, Cd, Cu, Mo, Pb and Zn were recorded in the soils collected around the Khatoon Abad smelter, especially in downwind directions, indicating the necessity of reclamation programs in the area. The concentration of these elements also decreased towards the depth which confirmed their anthropogenic inputs via Cu smelter.

The sequential extraction data revealed different partitioning patterns for the PTEs considered in this study. Cd and Zn were mainly associated with the carbonate fraction, As and Pb with the reducible fraction, Cu with the organic matter fraction and Mo with residual phase. PTE<sub>s</sub> chemical partitioning also showed notable differences in downwind directions. The more mobile fractions of the soils (i.e. exchangeable and carbonate fraction) have higher proportion in the vicinity of the smelter, especially in downwind direction, confirming the impact of smelting activity on the element's partitioning in the soils. The mobility of the elements may be classified in the following order: Cd > Zn > Pb > Cu > As > Mo. The highest mobility of Cd is expected, because Cd is generally presumed to be more mobile in polluted soils, compared to other PTEs. Investigations of the chemical element chemical partitioning in soil profile also indicated that the contaminants in the topsoil layer were bound in non-residual fractions to a greater extent than in the deeper parts of the profile, confirming their anthropogenic source in the study area.

On the basis of health risk assessment, the soils of the study area may pose non-carcinogenic and carcinogenic risks of As to the population (through ingestion pathway). The results of single extraction test confirmed this conclusion. The high concentration of target elements in the smelting wastes also pointed to the necessity of their proper disposal programs. In order to reduce the environmental risk in the study area, remediation activities are necessary.

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