



## In vitro bioaccessibility, phase partitioning, and health risk of potentially toxic elements in dust of an iron mining and industrial complex

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### ABSTRACT

Dust emitted from mining, ore processing, and tailing dumps have direct effects on miners who work close to these operations. The Gol-E-Gohar (GEG) mining and industrial company is one of the most important iron concentrate producers in the Middle East. The objective of the present study was to estimate the distribution, fractionation, and oral bioaccessibility of potentially toxic elements (PTEs) in dust generated by the GEG mining and industrial company. Total PTE content including Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, V, and Zn was quantified for suspended particulate matter (PM) in PM<sub>2.5</sub>, PM<sub>10</sub>, and total suspended particulate matter (TSP). As, Cd, Co, Cu, Fe, Ni, and Pb were quantified in fallout dust samples for oral bioaccessibility using in vitro Unified BARGE (UBM) Method and modified BCR fractionation analysis. Enrichment factors (EF) were calculated for the studied elements in PM; Cu, Fe, and As were found to be extremely enriched. Oral bioaccessibility of selected PTEs in fallout dust samples ranged from 0.35% to 41.55% and 0.06–37.58% in the gastric and intestinal phases, respectively. Regression modeling revealed that the bioaccessibilities of the PTEs could mostly be explained by total concentrations in dust particles. Average daily intake (ADI) calculations revealed that the intake of PTEs did not exceed the tolerable daily intake (TDI) values and as such was not considered a significant risk to workers. Additionally, the hazard quotients (HQ) and carcinogenic risk (CR) values were lower than the acceptable level. This study can provide further risk assessment and management of PTE pollution in occupational environments.

### 1. Introduction

Mining and processing of mineral commodities impact the environment by polluting air, water, and soil. These practices are known to generate large amounts of potentially toxic elements (PTEs), which can enter the body via their association with particulate matter through ingestion, inhalation, and dermal pathways thereby leading to serious health effects. The total (or pseudo-total) metal(loid) content in dust is usually taken into consideration for health risk assessment. However, not all of the PTE fraction in dust is available for absorption in the body (Cave et al., 2003). Thus, it is important to investigate bioavailability, which is the quantity of elements that reach the circulatory system and

human organs (Delbeke et al., 2020). Bioaccessibility is also defined as that portion of ingested/inhaled/dermal inorganic and organic substances potentially available to biological fluids. It is important to measure the bioaccessible fraction of contaminants rather than the total concentration to avoid overestimation in health risk assessment. Bioaccessibility tests are commonly performed by considering inhalation, ingestion, and dermal exposure pathways on broad geomaterial matrices including soil (van der Kallen et al., 2020), urban street dust (Huang et al., 2014), airborne particulate matter (Hu et al., 2012), tailing dust (Ettler et al., 2019), pure metal compounds, and metal alloys (Dutton et al., 2020). Oral bioaccessibility, as defined by Wragg and Cave (2003), is the fraction of a substance released from solid matrices into

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the gastrointestinal (GI) tract and potentially available to be released in bloodstream. Various approaches are proposed to estimate oral bio-accessible fraction of ingested contaminants. PTE risk assessments related to dust and/or soil ingestion for in vivo animal studies are time consuming, expensive, and raise ethical concerns. Hence, in vitro bio-accessibility assays are designed as surrogates to in vivo measurements, since they provide a good correlation with in vivo bioaccessibility experiments for some metal(loid)s (Basta and Juhász, 2014). There are several in vitro oral bioaccessibility methodologies, of which some such as simplified Bioaccessibility Extraction Tests (SBET) only mimic the condition of stomach. Such methods only provide “conservative” estimates as gastric solutions account only for solubilized metal ions, of which only a fraction is absorbed. While, biomimetic complete mouth–gastric– intestinal methods such as Physiologically Based Extraction Tests (PBET) simulate the whole digestive system. A more widely accepted PBET method is the one proposed by the BioAccessability Research Group of Europe (BARGE; BARGE INERIS, 2011).

The oral bioaccessibility of PTEs is affected by several factors including total concentration, geomaterial matrix and type, particle size, mineralogy, and physicochemical properties. Doysi et al. (2020) found that the 150–250  $\mu\text{m}$  size fraction in indoor dust bears the highest bio-accessible fraction for Cu, Ni, and Pb, while bioaccessibility of Cr, Mn, and Zn was highest in the < 45  $\mu\text{m}$  particle size. Dang et al. (2018) reported that the bioaccessibility of silver nanoparticles (AgNPs) increases with decreasing clay content and low pH. Ettler et al. (2020) demonstrated how mineralogy affects oral bioaccessibility in mining dust by reporting the highest oral bioaccessibility in readily soluble phases i.e., metal-rich Mn oxides, slag glass, hemimorphite, carbonates. However, relatively little research is done to investigate how the PTE distribution in dust fractions influences their bioaccessibility. The lack of such investigations is very obvious in developing countries, particularly in the Middle East. For this reason, the oral bioaccessibility of As, Cd, Co, Cu, Fe, Ni, and Pb of fallout dust is investigated during ore crushing, grinding, processing, and also from wind erosion on mine tailings and mine dumps in the Gol-E-Gohar (GEG) iron mine with nearly 5000 exposed employees to iron ore dust. For this purpose, simulated gastrointestinal fluids (i.e., stomach and small intestine fluids) using an in vitro BARGE UBM bioaccessibility test is used. To evaluate how the PTE distribution in dust fractions impacts oral bioaccessibility, the environmental As, Cd, Co, Cu, Fe, Ni, and Pb bioavailability in fallout dust is determined using modified BCR chemical extraction. The results of oral bioaccessibility are used to estimate PTE exposure risks via dust ingestion for employee/workers in the mining/ore processing industry. Furthermore, the concentration of PTEs including Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, V, and Zn in  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ , and TSP in indoor and outdoor sites is investigated to characterize the chemical profile of PTEs in a representative large iron mine. The results of this study are applicable to other similar mining and processing complexes around the world.

## 2. Materials and methods

### 2.1. Description of the study area

The GEG mining and industrial company is located 55 km southwest of Sirjan city (lat: 29°N, long: 55° 15' E) in the Kerman province of Iran. This company has about 1135 million tons total reserve of high-grade iron ore (with an ore grade of 57.2 wt% Fe) and is one of the most important iron concentrate producers in the Middle East with the annual production of up to 15 million tons of concentrate and more than 10 million tons of pellet (Barati et al., 2020). The GEG iron deposit comprises six separate ore bodies spanning an area of 40  $\text{km}^2$ . The climate of the study area is arid and semi-arid with an annual mean rainfall of 115 mm and annual mean air temperature of 18.1 °C. The prevailing wind direction is from the northeast (IRIMO, Sirjan Synoptic weather station).

### 2.2. Sample collection and preparation

In this study, both suspended particulate matter and fallout dust are collected from 10 sampling sites. In total, thirty PM samples were collected for  $\text{PM}_{2.5}$  (N = 10),  $\text{PM}_{10}$  (N = 10), and TSP (N = 10), in addition to 10 field blank filters. A single fallout dust sample was also collected from each site (N = 10). Samples were obtained inside of iron ore processing plants (six indoor sites) and outside (four outdoor sites) of main administrative buildings with high staff traffic (Fig. 1). Moreover, a site with the maximum distance of iron processing plants was selected as a clean ‘control’ location based on having the lowest PM mass and PTE concentrations. Table S1 in the Supplementary Information (SI) shows detailed information about geographic coordinates of each sampling sites. For PM sampling, a low-volume PM sampler (Techora, Italy) was employed at 10 sampling stations. All samples in  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ , and TSP were collected over 24-h on a given sampling day between Dec 2014 and May 2015. PTFE membrane filters of 2.00  $\mu\text{m}$  pore size and 46.2 mm diameter with supporting ring (Tisch Scientific, USA) were used to collect the PM fractions with a flow rate of 16–17  $\text{L min}^{-1}$ . The filters were coated with a very thin layer of grease to prevent PM bounce.

Dry fallout dust samples were collected simultaneously using a plastic collection pan-and-hand brush swabbing across a clean non-porous collection surface with 100- $\text{cm}^2$  surface area, placed at 1–2 m above the ground. Samples were dried at room temperature for several days in a clean space in the laboratory, and then were homogenized and passed through both a mesh #10 (< 2 mm) and a mesh #60 (< 250  $\mu\text{m}$ ) sieve in order to measure the physico-chemical properties and the total and bioaccessible concentration, respectively.

### 2.3. Mass and elemental concentration of PM

Mass concentration of the collected PM was determined by the difference between initial and final weights of filters before and after sample collection with a duration time of 24 h (USEPA, 1999). PTFE filters were weighed using an electron analytical microbalance (Model LIBROR AEL-40SM; SHIMADZU Co., Kyoto, Japan) with 1  $\mu\text{g}$  sensitivity. Prior to initial and final weighings, filter papers were placed in a desiccator containing dry silica after being equilibrated for 24 h at an ambient temperature of  $20 \pm 1$  °C and relative humidity (RH) of  $20 \pm 5\%$  to eliminate the influence of RH on PM measurements.

The exposed filters were analyzed for their PTE concentrations using inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Nexion 300 ICP MS, USA) at LabWest Minerals Analysis Pty Ltd, Australia. Approximately 0.1 g of sample was digested in a microwave-assisted system (Anton Paar MW3000 microwave digester, Graz, Austria) using a mixture of  $\text{HNO}_3$ , HCl, and HF at 170 °C and 1.8 MPa for 40 min. Hydrofluoric acid was complexed and the sample solution was brought up to final volume of up to 25 mL using distilled water. The solution was presented to ICP-MS for determination of required analytes. The detection limits for PTEs are presented in the Table S2 in the SI.

### 2.4. Fallout dust characterization

Fallout dust grain size analysis for dust texture determination was conducted using a standard hydrometer method. Dust pH measurements were performed using a recognized standard protocol with calcium chloride ( $\text{CaCl}_2$ ) (Fisher Scientific, UK) at 0.01 M and a dust:solution ratio of 1:10 using a glass slurry electrode and Orion SA720 meter pH meter (UK). Organic matter content (OM) was estimated by calculating the loss on ignition (LOI) at a specified temperature of 450 °C (Johnson, 2011). For total element concentrations, briefly, 0.25 g of the homogenized dust samples was digested (in triplicate) based on a mixed acid digestion approach including HF,  $\text{HNO}_3$ , and perchloric acid ( $\text{HClO}_4$ ) (Green et al., 2006). An Agilent 7500cx ICPMS instrument fitted with a CETAC ASX-520 autosampler was used for analysis of total elemental digests. Sample introduction from the autosampler to the ICP-MS was

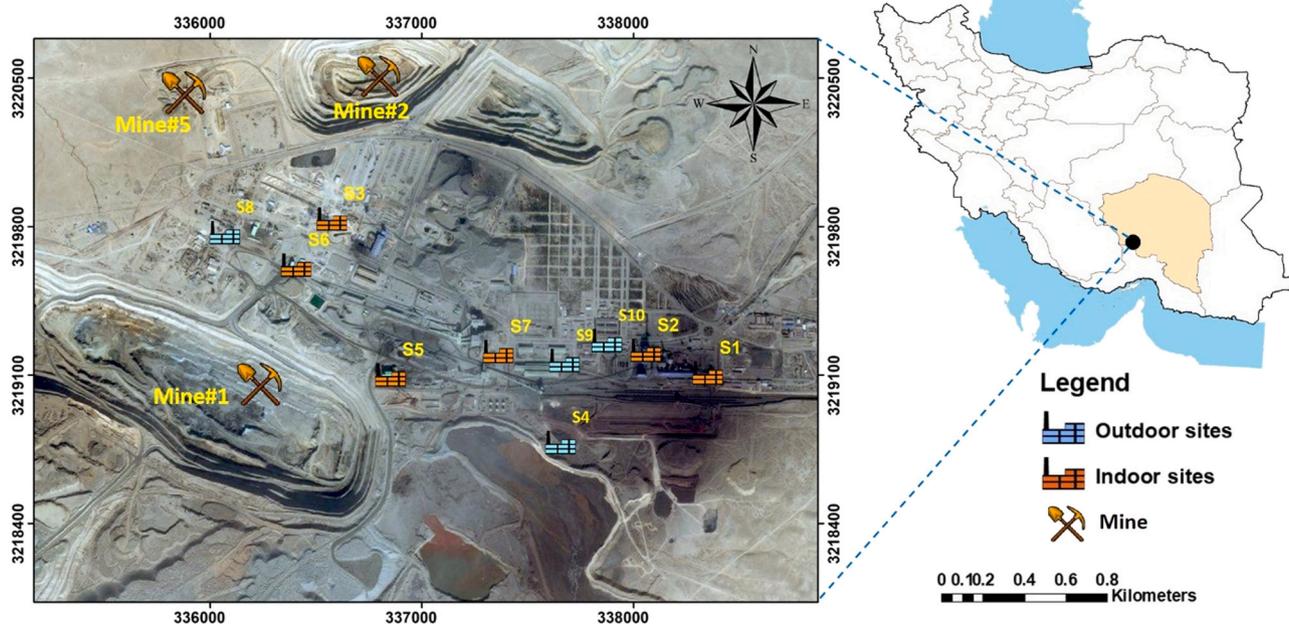


Fig. 1. Map showing the locations of the mining and processing plants in the study area. Suspended particulate matter in  $PM_{2.5}$ ,  $PM_{10}$ , TSP, and fallout dust samples were collected from indoor (S1: IPP<sub>1</sub>, S2: IPP<sub>2</sub>, S3: PLY, S4: HRP, S5: PC, S6: ICP) and outdoor sites (S7: TB, S8: MOO, S9: R&D center, S10: B No. 45) of the iron ore processing plants and official buildings. See Table S1 for abbreviations.

controlled by a CETAC ASXpress + vacuum pump. Quantitative data analysis was performed using MassHunter Workstation software (Agilent).

## 2.5. Oral bioaccessibility method

Oral bioaccessible fractions were determined for selected PTEs (As, Cd, Co, Cu, Fe, Ni, Pb) using the in vitro Unified BARGE Method (UBM) according to ISO Technical Specification 17924:2018 standard. The UBM test is carried out on 0.6 g of dried and sieved (< 250  $\mu\text{m}$ ) fallout dust samples ( $N = 5$ ). The samples were further sieved to < 250  $\mu\text{m}$  as this fraction commonly taken to be the optimum size for both adherence to human hands or skin and easily inhaled or ingested (Kajiwara and Takigami, 2016).

The simulation was carried out at  $37 \pm 2$  °C (human body temperature), under fasting conditions through three different stages involved in digestion: mouth (extraction time: 5 min, pH of  $6.5 \pm 0.5$ ), stomach (1 h, pH of 0.9–1.0 with a final pH of 1.2) and small intestinal cavities (4 h, pH of  $6.3 \pm 0.5$ ) using daily prepared simulated saliva (S) and gastric (G) fluids and bile (B) plus duodenal (D) fluids to represent the intestinal fluid. The preparation of each fluid requires the preparation of two solutions (one inorganic (I) and one organic solution (O)). Each fluid (S, G, D or B) results from the combination of one inorganic solution, one organic solution, and specific enzymes. Table S3 summarizes the weight (mg) or volume (mL) of each reagent required for the preparation of 250 mL of each solution (I and O) for a final volume of each fluid reaching 500 mL (I+O) (Mombo et al., 2016). The analysis includes two individual sequential extracts per test: gastric (G), consisting of an extraction solution removed from the system after completion of the saliva followed by the gastric phase; and gastrointestinal (GI), representing the extraction solution removed after simulation of the mouth, stomach, and intestinal phases using simulated saliva and gastric phases, followed by extraction under small intestinal conditions using simulated bile and duodenal fluids of the system. All solvents were analytical grade and purchased from Sigma (UK), Merck (UK), J.T. Baker (UK), or Fluka (Germany). Both digests for total elemental content, and UBM extracts were analyzed using an Agilent 7500cx ICP-MS instrument. The bio-accessible fraction (%BAF) in the dust samples was calculated using the

following equation:

$$BAF(\%) = \frac{Element_{bioaccessible}}{Element_{total}} \times 100 \quad (1)$$

where  $Element_{bioaccessible}$  is bioaccessibility concentration in both G and GI phases, separately.

## 2.6. Sequential extraction analysis

A four-step modified BCR sequential extraction scheme developed by Yan et al. (2010) was applied on ten fallout dust samples to evaluate fractionation and environmental availability of As, Cd, Co, Cu, Fe, Ni, and Pb, following previous work (Malferrari et al., 2009). The PTE concentration in each step was detected using inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent model 735, USA) at Zarazma Mineral Studies Company in Iran.

The recovery percentage (R (%)) of the chemical sequential extraction was determined using the following equation:

$$R(\%) = \frac{(C_{fraction\ 1} + C_{fraction\ 2} + C_{fraction\ 3} + C_{fraction\ 4})}{C_{pseudototal\ digestion}} \times 100 \quad (2)$$

The recoveries of As, Cd, Co, Cu, Fe, Ni, and Pb were in the ranges of 81.5–133.5%, 98.5–127.7%, 73.3–84.1%, 76.6–94.9%, 123.1–128.7%, 71.6–84.0%, and 113.3–122.8%, respectively. These results showed that the fractionation procedure was sufficiently accurate.

The relative index of PTE mobility was determined using the mobility factor (MF) as follows (Kabala and Singh, 2001):

$$MF = \frac{F1}{F1 + F2 + F3 + F4} \times 100 \quad (3)$$

where F1, F2, F3, and F4 were concentration of PTEs in the different fractions including acid soluble (F1; e.g., carbonates), reducible (F2; e.g., amorphous iron/manganese oxides and hydroxides), oxidizable, (F3; e.g., organic matter and sulfides) and residual (F4; e.g., silicate bound metals).

## 2.7. Quality control (QC)

Table S2 in the SI summarizes the details of values for analysis of certified reference materials (CRM), recovery, and the measured detection limits in each sample matrix. Method validation of PTE content in PM samples by ICP MS was performed by measuring blank reagents (ratio 1:20), analytical duplicates (ratio 1:20), and CRM (ratio 2:20) including STD OREAS920st5, OREAS151ast3, OREAS45dst4, and DC73309st2. The recovery rate of the PTEs ranged between 88.2% and 114.5% (Table S2 in the SI), indicating reasonable agreement between the measured and certified concentrations. All blank extractions returned values below the method detection limits. For the QC of the UBM, NIST2711a (Montana Soil II) and BGS-102 were used for total elemental concentrations. Moreover, within every batch, of a maximum of five unknown samples, one duplicate, one reagent blank, and one international standard reference materials (SRM) including BGS-102 was used. Blank extractions were all below the detection limit. pH calibration solutions are analyzed before and after every 5 fallout dust suspensions using a pH 7 buffer solution and at least one unknown sample was measured in duplicate every 5 samples. For the modified BCR sequential extraction procedure, a certified reference material (GBW 7312) and a reagent blank were employed. An internal check was performed for fractionation analysis by comparing the total amount of PTEs extracted in different fractions with the results of the pseudo-total digestion.

## 2.8. Enrichment factor (EF)

Enrichment factor (EF) was used to assess whether the PTE concentrations in the PM samples were enriched relative to crustal matter (Cao et al., 2008) using the following equation:

$$EF = \frac{(X_i/Al)_{samples}}{(X_i/Al)_{crust}} \quad (4)$$

where  $X_i$  indicates the PTE concentration in the airborne particulate sample relative to average concentrations in crustal material (Rudnick and Gao, 2003). For EF calculation, Al was selected as the reference element, assuming that the contribution of its anthropogenic sources to the atmosphere is negligible as has been done in past studies (Ma et al., 2019).

## 2.9. Exposure assessment

Risk assessment with exposure to iron ore dust via ingestion was carried out to evaluate both non-carcinogenic and carcinogenic toxic risks. The calculation corresponded to an estimate of occupational exposure of miners and employees working inside the company. Exposure was expressed in terms of the average daily intake (ADI) and was calculated separately for each PTE and for ingestion exposure route (Equations (A-1), in SI). The potential non-carcinogenic hazard quotients for oral ingestion ( $HQ_{ingestion}$ ) were subsequently calculated by Equation (A-2 in the SI) as the ratio of the exposure of each PTE (daily intake) and the level at which no adverse effects are expected. The carcinogenic risk (CR) was calculated according to equation (A-3 in the SI) (USEPA, 1989). Parameters used in all equations are defined in the SI.

## 2.10. Statistical analysis

The experimental data was treated statistically using SPSS software (version 24.0) and Minitab (version 18). The Kruskal-Wallis non-parametric tests were applied to verify the significance of possible differences between PTE concentrations in PM samples. To study both the site-effect and digestibility effect, generalized linear model multivariate analysis of variance (GLM MANOVA) was applied. Stepwise linear

regression (SWLR) was used to reveal the most effective factors on gastric and gastrointestinal bioaccessibility of each element, including total concentration, available and residual fraction, and physicochemical properties.

## 3. Results and discussion

### 3.1. Physicochemical characteristics of the dust samples

The physicochemical characteristics of fallout dust samples are given in Table S4. Dust samples have similar pH values ranging from neutral (7.12) to alkaline (8.50), with a mean of 7.59. The high pH in D1 is the result of adding limestone as a fluxing agent to increase adherence of the iron ore pellet in the iron ore pelletizing plate during metallurgical production of iron ore. Organic matter content ranged from 0.25% to 0.65% (on mass basis) with a mean of 0.53%. Dust samples showed a sandy-silty texture with a mean of 60.1% w/w of sands, 32.7% w/w of silt, and only 7.2% of clay. The sandy textures of fallout dust particles, mostly composed of coarse particles, could be explained by assuming an anthropogenic origin as a result of grinding and crushing of iron ore.

### 3.2. Particulate matter mass and PTE concentrations

As shown in Table 1, the mean ( $\pm$ standard deviation, SD) mass concentration was  $2.31 \pm 2.12 \text{ mg m}^{-3}$  for  $PM_{2.5}$ ,  $14.73 \pm 15.08 \text{ mg m}^{-3}$  for  $PM_{10}$ , and  $63.54 \pm 72.74 \text{ mg m}^{-3}$  for TSP in indoor sampling sites. The daily  $PM_{2.5}$  and  $PM_{10}$  mass concentrations were 66 and 98 times higher than the US National Ambient Air Quality Standard (NAAQS) 24-h standard of 35 and  $150 \mu\text{g m}^{-3}$ , respectively. Higher mass loadings of PM were observed in indoor sampling sites (especially in ICP and IPP) due to the large volume of emissions by dry grinding of iron ore and inadequate ventilation inside the plants in contrast to the wind diluting effect and dispersion of PM at outdoor sites. The main industrial processes in indoor sites are iron ore grinding and crushing, which produce particles with a relatively larger size, which, in turn, result in relatively lower airborne concentration of fine particles. Concentration of measured PTEs in  $PM_{2.5}$ ,  $PM_{10}$ , and TSP for the ten sampling sites (indoor and outdoor sites) are reported in Table 1. The Kruskal–Wallis test showed significant differences ( $p < 0.05$ ) between indoor concentrations of Al, Co, Mn, and Mo in  $PM_{2.5}$ ,  $PM_{10}$ , and TSP samples. Similar to mass concentration, PTE concentrations at indoor sites for the 3 PM size ranges examined were higher than those for outdoor sites.

PTE content in PM is significantly influenced by various factors related to both indoor and outdoor conditions. At outdoor sites, higher wind speeds decrease PTE content due to higher diluting associated with more aggressive dispersion. Copper, Fe, V, Co, Ni and Zn were the most abundant PTEs for all PM size ranges for indoor and outdoor sites.

Iron had the highest average indoor concentrations:  $0.62 \pm 0.77$ ,  $3.30 \pm 3.40$ , and  $4.55 \pm 8.35 \text{ mg m}^{-3}$  for  $PM_{2.5}$ ,  $PM_{10}$ , and TSP, respectively. The average Cu concentrations for indoor  $PM_{2.5}$ ,  $PM_{10}$ , and TSP were  $0.82 \pm 1.07$ ,  $5.18 \pm 7.61$ , and  $8.01 \pm 16.75 \mu\text{g m}^{-3}$ , respectively. Similar concentrations of PTEs were also reported in tailings and topsoil samples in the study area in past work (Soltani et al., 2017a). This suggest that iron ore mineralization, mining, and extraction in the area have a significant influence on PTEs released in the surrounding environment. These emitted PTEs from several units such as the pelletizing plant and the smelting furnace in iron and steel manufacturing should be considered as marker elements for iron and steel production emission. Elemental concentrations of PM emitted from industrial sites are affected by multiple factors including ore chemistry, ore treatment method, PM sizes, and distance from mining and ore processing sites. According to geochemical and geochronological data, the GEG iron ore is categorized as an iron oxide copper gold (IOCG) type with an epigenetic hydrothermal origin (Jafari et al., 2019). The IOCG deposits are generally rich in elements like Cu, Fe, Co, Ni, and V

**Table 1**  
Concentration of PM mass and PTEs in PM<sub>2.5</sub>, PM<sub>10</sub>, and TSP samples collected from GEG indoor and outdoor sites.

Analyte/fraction	PM <sub>2.5</sub> (n = 10)						PM <sub>10</sub> (n = 10)						TSP (n = 10)					
	Indoor			Outdoor			Indoor			Outdoor			Indoor			Outdoor		
	Mean±SD	Min	Max	Mean±SD	Min	Max	Mean±SD	Min	Max	Mean±SD	Min	Max	Mean±SD	Min	Max	Mean±SD	Min	Max
PM Mass (mg m <sup>-3</sup> )	2.31 ± 2.12	0.06	0.01	0.06 ± 0.06	0.03	0.13	14.73 ± 15.08	2.38	46.51	0.23 ± 0.10	0.13	0.33	63.54 ± 72.74	0.05	197.22	1.92 ± 1.56	0.82	3.02
Al (µg m <sup>-3</sup> )	24.1 ± 31.8	0.46	86.22	2.68 ± 3.78	0.43	7.04	247.3 ± 401.3	9.48	1138	3.92 ± 1.23	3.18	5.35	428.5 ± 916.6	13.74	2502	33.21 ± 37.33	6.82	59.61
As (ng m <sup>-3</sup> )	46.2 ± 53.8	1.30	149.3	1.75 ± 1.02	0.65	2.65	214.3 ± 250.2	20.11	692.8	6.53 ± 6.06	2.62	13.51	306.1 ± 627.1	23.17	1726	18.22 ± 20.93	3.42	33.02
Cd (ng m <sup>-3</sup> )	0.15 ± 0.12	0.03	0.32	0.08 ± 0.03	0.04	0.10	0.67 ± 0.90	0.03	2.57	0.14 ± 0.16	0.04	0.32	0.49 ± 0.88	0.07	2.47	0.14 ± 0.16	0.03	0.25
Co (ng m <sup>-3</sup> )	138.8 ± 166.1	2.26	426.1	1.45 ± 1.95	0.17	3.70	1160 ± 1891	67.06	5375	5.28 ± 3.04	2.93	8.71	2517 ± 5677	125.2	15380	100.8 ± 128.7	9.82	191.8
Cr (ng m <sup>-3</sup> )	144.3 ± 233.1	2.03	652.6	8.08 ± 6.24	4.01	15.27	636.8 ± 838.2	17.47	2367	9.20 ± 1.34	7.94	10.61	886.8 ± 1787	33.63	4932	65.44 ± 72.77	13.98	116.9
Cu (µg m <sup>-3</sup> )	0.82 ± 1.07	0.02	2.65	0.009 ± 0.008	0.004	0.03	5.18 ± 7.61	0.29	21.59	0.03 ± 0.01	0.02	0.04	8.01 ± 16.75	0.39	45.91	0.37 ± 0.46	0.04	0.69
Fe (mg m <sup>-3</sup> )	0.62 ± 0.77	0.01	1.75	0.004 ± 0.003	0.001	0.008	3.30 ± 3.40	0.23	8.41	0.016 ± 0.01	0.011	0.024	4.55 ± 8.35	0.39	23.38	0.4 ± 0.51	0.04	0.76
Hg (ng m <sup>-3</sup> )	0.48 ± 0.68	0.05	1.90	0.05 ± 0.04	0.03	0.10	1.59 ± 3.10	0.06	8.58	0.04 ± 0.01	0.02	0.05	0.82 ± 1.41	0.07	3.90	0.11 ± 0.11	0.03	0.19
Mn (µg m <sup>-3</sup> )	0.57 ± 0.65	0.01	1.70	0.04 ± 0.05	0.01	0.10	4.55 ± 6.71	0.24	19.46	0.06 ± 0.02	0.05	0.08	7.11 ± 14.30	0.44	39.44	0.58 ± 0.70	0.09	1.08
Mo (ng m <sup>-3</sup> )	4.43 ± 4.61	0.34	11.59	0.14 ± 0.13	0.03	0.29	24.08 ± 25.99	2.64	77.88	0.52 ± 0.33	0.28	0.89	41.91 ± 86.95	3.90	238.9	2.59 ± 3.12	0.38	4.79
Ni (ng m <sup>-3</sup> )	210.5 ± 237.5	2.71	619.1	5.22 ± 5.90	1.79	12.03	1316 ± 1628	60.65	4811	9.15 ± 3.11	6.42	12.53	2125 ± 4388	131.9	12052	113.7 ± 137.8	16.26	211.1
Pb (ng m <sup>-3</sup> )	16.39 ± 11.60	3.55	30.89	5.08 ± 2.97	1.90	7.79	59.28 ± 70.89	3.35	205.65	10.47 ± 11.38	3.44	23.60	77.81 ± 167.3	4.52	456.9	12.44 ± 12.54	3.57	21.30
V (ng m <sup>-3</sup> )	401.4 ± 507.8	4.51	1171	7.55 ± 8.26	1.88	17.03	2543 ± 2668	117.0	6012	19.06 ± 4.55	14.48	23.58	2803 ± 4966	243.5	14011	364.4 ± 458.0	40.59	688.3
Zn (ng m <sup>-3</sup> )	241.13 ± 330.0	12.25	951	22.40 ± 8.97	17.17	32.76	852.5 ± 1021	57.20	3056	26.93 ± 11.69	19.04	40.36	1084 ± 2202	94.18	6071	133.0 ± 150.9	26.30	239.8

Note: n = number of analyzed PM samples, SD = standard deviation, min = minimum, and max = maximum.

(Belperio and Freeman, 2004). Jafari et al. (2019) reported elevated concentrations of the transition elements such as Co, V and Ni in magnetite, the major ore mineral in the GEG mineralization area. Compared with PTE occupational/industrial limits (NIOSH) and Air Quality guidelines issued by the US Environmental Protection Agency (USEPA), the European Commission Air Quality Standards, and the World Health Organization (WHO) (Table S5), the mean concentrations of As, Cr, Co, Mn, and Ni in the 3 PM size ranges exceeded recommended safe limits. The comparison of PM mass and PTE concentration in different sampling sites are shown in Table S6 in the SI. The maximum concentrations of the aforementioned PTEs in PM<sub>2.5</sub>, PM<sub>10</sub>, and TSP were associated with the highest mass concentrations of particulate matter, including in particular inside the ICP and IPP. The maximum concentrations of all PTEs were measured in TSP samples inside the ICP: Fe (23.38 mg m<sup>-3</sup>) > Al (2502 µg m<sup>-3</sup>) > Cu (45.91 µg m<sup>-3</sup>) > Mn (39.44 µg m<sup>-3</sup>) > Co (15380 ng m<sup>-3</sup>) > V (14011 ng m<sup>-3</sup>) > Ni (12052 ng m<sup>-3</sup>). In contrast, the minimum PM mass and PTE concentrations were measured in site #S10 (B. No. 45) owing to its greater distance from the iron ore processing plants (Table S6). The results of Kruskal-Wallis test showed a significant difference (p < 0.05) in As, Cd, Cr, Hg, Mo, Ni, Pb, V, and Zn concentration as well as PM mass concentration among 10 sampling sites due to their different processing activities.

Higher mass concentrations are the result of dry grinding of iron ore and inadequate ventilation. Smaller particles are able to cross blood-lung barrier and cause serious health hazards due to their greater ability to penetrate deeper into the lower airways (Capello and Gaddi, 2018).

The results of calculated EF for the PTEs in PM samples are shown in Fig. S1. The results indicate a significant enrichment (higher than 20) in Cu, Fe, As, and Co in 3 PM sizes. In contrast, Cr and Mn were found negligibly enriched in all PM size ranges. Some PTEs such as As, Cr, Cu, Mo, Ni, Pb, and Zn were enriched more in PM<sub>2.5</sub> fraction, whereas, Co, Fe, and Mn were more enriched in TSP samples. This also indicates that the exposure to fine particles in this area can have more adverse health effects associated with As, Cu, Ni, and Zn. Schleicher et al. (2012) reported higher EFs for PTEs in PM<sub>2.5</sub> as compared to TSP, indicative of the influence of anthropogenic sources, which are specifically higher in finer particles.

### 3.3. Total and bioaccessible concentrations of PTEs in fallout dust

Seven PTEs (As, Cd, Co, Cu, Fe, Ni, Pb) were detected in the < 250 µm particle size fraction of fallout dust (Table 2). The total concentrations of these elements in descending order were as follows: Fe (380.7 g kg<sup>-1</sup>) > Cu (236.8 mg kg<sup>-1</sup>) > Co (102.5 mg kg<sup>-1</sup>) > Ni (99.33 mg kg<sup>-1</sup>) > As (11.46 mg kg<sup>-1</sup>) > Pb (2.10 mg kg<sup>-1</sup>) > Cd (0.05 mg kg<sup>-1</sup>). Elevated concentrations of Fe, Co, Cu, and Ni could be explained by the iron ore mineralization in the area and occurrence of these elements. Copper, Co, Ni, and As are also enriched in soil

**Table 2**

Total and bioaccessible concentration (±SD) in gastric and gastrointestinal fractions of selected PTEs in mg kg<sup>-1</sup> (except for Fe in g kg<sup>-1</sup>) for fallout dust samples, SD= Standard deviation, %BAF= bioaccessible factor (n = 5).

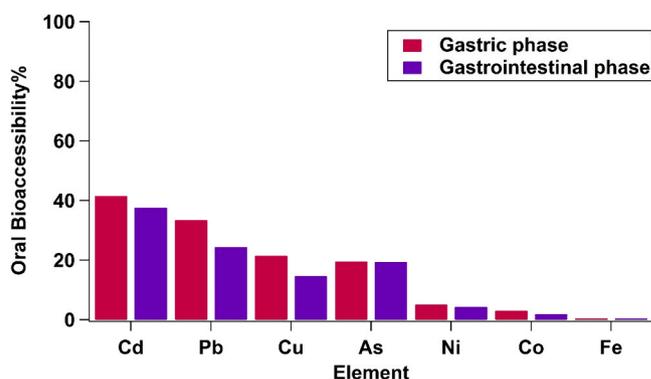
Element	Total Concentration				In-vitro gastro-intestinal extraction			
	Mean ± SD	Min	Max	Median	Phase I (Gastric digest)		Phase II (Gastric+Intestinal digest)	
					Mean ± SD	% BAF	Mean ± SD	% BAF
As (mg kg <sup>-1</sup> )	11.46 ± 5.85	2.69	18.34	12.12	2.24 ± 1.25	19.53	2.23 ± 1.12	19.43
Cd (mg kg <sup>-1</sup> )	0.05 ± 0.02	0.035	0.08	0.04	0.022 ± 0.011	41.55	0.020 ± 0.009	37.58
Co (mg kg <sup>-1</sup> )	102.5 ± 62.98	31.18	204.0	95.96	3.10 ± 1.58	3.02	2.02 ± 0.94	1.97
Cu (mg kg <sup>-1</sup> )	236.8 ± 124.4	61.95	364.5	212.2	49.04 ± 22.30	21.43	31.79 ± 13.47	14.64
Fe (g kg <sup>-1</sup> )	380.7 ± 212.3	145.0	707.8	307.2	0.97 ± 0.31	0.35	0.18 ± 0.08	0.06
Ni (mg kg <sup>-1</sup> )	99.33 ± 28.37	57.74	126.0	103.0	5.04 ± 2.02	5.07	4.32 ± 1.83	4.35
Pb (mg kg <sup>-1</sup> )	2.10 ± 1.41	0.90	4.50	1.79	0.70 ± 0.81	33.43	0.51 ± 0.20	24.41

Note: SD = standard deviation, %BAF = bioaccessible factor.

surrounding the study area (Soltani et al., 2017a). The trend of mean bioaccessible concentrations in the simulated gastric fluids (phase I) was as follows: Fe (0.97 g kg<sup>-1</sup>) > Cu (49.04 mg kg<sup>-1</sup>) > Co (3.10 mg kg<sup>-1</sup>) > Ni (5.04 mg kg<sup>-1</sup>) > As (2.24 mg kg<sup>-1</sup>) > Pb (0.70 mg kg<sup>-1</sup>) > Cd (0.022 mg kg<sup>-1</sup>). Also, the mean bioaccessible concentration of these elements in gastrointestinal phase (phase II) showed the following decreasing trend: Fe (0.18 g kg<sup>-1</sup>) > Cu (31.79 mg kg<sup>-1</sup>) > Ni (4.32 mg kg<sup>-1</sup>) > As (2.23 mg kg<sup>-1</sup>) > Co (2.02 mg kg<sup>-1</sup>) > Pb (0.51 mg kg<sup>-1</sup>) > Cd (0.020 mg kg<sup>-1</sup>). The difference of bioaccessibility between PTEs is probably as a results of various chemical forms of metals in soil which they are bound to (Pelfrène et al., 2011). The concentration of these elements were higher in the gastric stage. In the neutral or weak alkaline environment of the intestine, the higher pH and increased concentration of a number of enzymes lead to metal stabilization resulting in lower bioaccessibility values. Chemical stabilization occurs by re-adsorption of elements onto particle surfaces, complexation by pepsin, and precipitation of these elements as relatively insoluble compounds from solution. Gu and Gao (2018) found higher gastric bioaccessibility of Cd, Pb, Cu, Zn, and Fe than intestinal fractions in the park soils of Guangzhou, China. Similar findings were obtained by Dean et al. (2020).

During the gastrointestinal phase extraction, dissolved Cd in the gastric phase may be co-precipitated with Fe or adsorbed onto Fe oxide (Luo and Tu, 2018). In the GI tract, from the stomach to the intestine, Cu and Ni are mainly stabilized by complexation with available organic ligands (Ren et al., 2015). Yang et al. (2003) showed that solubility of Pb in simulated biofluids substantially decreased in the intestinal fluids. Furthermore, complexes of As in the gastric phase may not be affected by the pH in the intestinal environment, showing similar bioaccessibility in both phases (Fig. 2).

Table 2 summarizes the percentile values across the calculated BAFs for individual PTEs in the first and second phases, respectively. Cadmium and Pb, with the lowest total concentrations of 0.05 and



**Fig. 2.** Oral bioaccessible factor (BAF%) of mean concentration of selected PTEs in gastric and gastrointestinal phases in fallout dust (FD) samples.

2.10 mg kg<sup>-1</sup>, respectively, generally had the highest %BAF in gastric and gastrointestinal phases compared to other PTEs in this study. [Morman et al. \(2009\)](#) reported a decreasing bioaccessibility trend of Cd > Pb > Ni > As > Cr in < 250 µm and < 2 mm fractions of twenty soil samples from broad transect across the United States and Canada. Iron showed the most total concentration and the least %BAF in two phases. Previous studies have demonstrated that the origin and mineralogy of geo-material can affect PTE bioaccessibility. Results from x-ray diffraction (XRD) analyses of GEG dust ([Soltani et al., 2017b](#)) indicated that the Fe distribution in the mineral phases of fallout dust samples are associated with oxide and sulfide minerals including magnetite (Fe<sub>3</sub>O<sub>4</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>), and pyrite (FeS<sub>2</sub>), all of which exhibit low solubility in gastrointestinal fluids ([Ruby et al., 1999](#)). Furthermore, Fe mainly remained in the residual fraction (crystalline structure of the dust particles), which would also not be bioavailable and hard to be extracted in the gastrointestinal solution.

### 3.4. Fractionation of PTEs in fallout dust

The fractionation pattern of PTEs in the fallout dust, using the modified BCR sequential extraction is shown in [Table S7](#) and [Fig. 3](#). The results showed that the quantities of PTEs in the first three non-residual fractions (F1+F2+F3) were low except for Cd and Cu, meaning that a greater part remains in the residual fraction of the fallout dust. The first three fractions accounted for 30.05%, 53.49%, 15.26%, 42.22%, 9.33%, 32.13%, and 30.81% of the total As, Cd, Co, Cu, Fe, Ni, and Pb, respectively. These fractions may be regarded as the most mobile, and hence potentially bioavailable, representing significant risks to the environment ([Davutluoglu et al., 2011](#)). The highest content of As (69.95%), Ni (67.87%), and Pb (69.19%) was partitioned in the residual fraction followed by the second phase classified as “bound to Fe/Mn oxides”. Arsenic extracted from the first three fractions occurred in the sorption sites of each specific compartment, while As extracted in the residual fraction was linked to dissolution of iron precipitates (Fe-As compound or co-precipitates) ([Kim et al., 2003](#)). Thus, the majority of As was in the Fe-As precipitates or co-precipitates. [Dong et al. \(2013\)](#) confirmed that Ni is mainly present in the Fe-Mn oxides phase. [Zajzon et al. \(2013\)](#) reported that significant Pb content bound in the magnetite lattice structure contributed to the residual fraction of TSP samples collected from a steel factory in Hungary.

A fair portion (46.51%) of Cd was found in F4, with 12.14% in the oxidizable fraction (F3), 21.71% in the reducible fraction (F2), and 19.64% in the acid soluble fraction (F1). The proportion of the first three fractions was high and up to 53.49% of the total Cd, indicating high potential mobility of this element in fallout dust samples. Since it is known to be toxic, its concentration in the bioavailable fractions causes an environmental hazard. [Sipos et al. \(2016\)](#) found the majority of the

Cd was tied up with non-residual fractions in mine tailings and TSP, respectively.

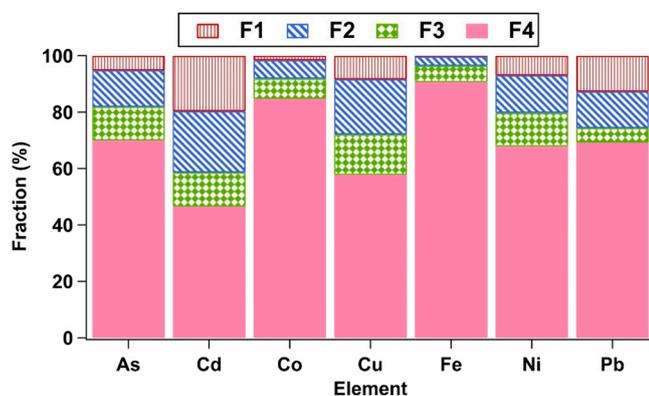
Among other analyzed elements, Cu has a larger share (14.38%) associated with the oxidizable fraction. Copper has a high adsorbing capacity for organic matter by a strong stable complexation ability of Cu<sup>2+</sup> cations with organic matter ([Audry et al., 2006](#)). Furthermore, Cu, as a chalcophile element also has an affinity for sulfur and in nature is mainly bounded to sulfides ([Tüzen, 2003](#)). However, the OM content of the FD samples is very low, and Cu is probably bound to sulfides rather than OM.

The Fe and Co association in different fractions followed the sequence: F4 > F3 > F2 > F1. Up to 90% of Fe and 84% of Co were bounded strongly in the dust matrix, predominantly in the residual fraction. Similar results are also reported by [Iwegbue \(2013\)](#). The higher percentage of Fe and Co in the residual fraction suggested a relatively higher share of natural sources (natural occurrence of iron ore in GEG area), indicating that under changing environmental conditions these elements in fallout dust samples are less bioavailable. Iron and Co are lithogenic and are probably associated with primary and secondary aluminosilicates, sulfide, and crystallized oxide minerals ([Han, 2007](#)). Iron is mostly present in the crystalline forms such as hematite (Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>). A previous study by [Soltani et al. \(2017b\)](#) demonstrated that iron ore dust was rich in principal minerals including magnetite, hematite, and pyrite in the GEG mine.

The calculated MFs for PTEs in the present study are summarized in [Table S7](#). The mobility of PTEs in fallout dust samples decreased in the following trend: Cd > Pb > Cu > Ni > As > Co > Fe. The MFs were comparatively higher in Cd with a mean value of 19.75%, followed by Pb (11.57%), while Fe (0.23%) and Co (1.58%) may be regarded as the most stable elements in the samples due to their low MFs. High MFs have already been explained as high lability and bioavailability of PTEs in studied samples, which may create a serious risk to the environment matrices via increasing accumulation in soils and plants. Fractionation results indicated that the PTE distribution in the four fractions was similar. Most PTEs were retained within the crystal lattices or inside crystallized oxides, which is considered to contain lithogenic forms, suggesting their presence in very resistant phases ([Singh et al., 1998](#)). However, in the acidic medium of stomach (pH < 1.5), PTEs bound to mobile fractions (F1–F3) may be absorbed, depending on their bioavailability ([Csavina et al., 2012](#)). Furthermore, deposition of PTEs bearing dust and uptake by soil and plants may cause potential health effects through contaminated plant consumption. Nomads usually move in the vicinity of the GEG area during warm periods of the year and their livestock graze on native plants, so they are potentially at risk of PTEs exposure through the food chain.

### 3.5. Factors related to PTE oral bioaccessibility

Results of the GLM MANOVA test ([Table S8](#)) verified that there are significant differences between the effects of predictors on the values of different elements in both of gastric (G) and gastrointestinal (GI) phases (p < 0.05). Moreover, results confirmed that the site effect was not significant (p > 0.05). In other words, the effects of predictors on G and GI should be separately studied for each element. For this purpose, the importance of each factor on G and GI bioaccessibility was examined with SWLR modeling. In this analysis, G and GI were the response variables. Also total concentration (TC), OM, pH, sand, silt, clay, available fraction (AF, in abbreviation including F1+F2+F3), and residual fraction (RF=F4, in abbreviation) were continuous predictors. [Table 3](#) summarizes the results of the simultaneous effects of different factors on G and GI in SWLR models for the different elements. For As, Cu, Co, Fe, and Ni, only TC was included in SWLR (p < 0.05). In other words, TC was the only statistically significant independent variable and other factors were excluded. In the gastric phase, the ability of the fitted model to predict was 99.9%, 95.7%, and 97.0% for As, Cu and Ni, respectively. For Cd, only AF was included in SWLR and could determine 99.0% of



**Fig. 3.** Percentage distribution of selected PTEs in the different fractions based on modified BCR sequential extraction (F1: acid soluble; F2: reducible; F3: oxidizable; F4: residual).

**Table 3**

The results of stepwise linear regression (SWLR) models to determine the most important factors impacting G and GI bioaccessibility for each element.  $b_i$  = model's parameters (coefficients); SE = standard error; Beta = standardized model's parameters; t = t statistic; p = p value, R Square = coefficient of determination, TC = total concentration; AF = available fraction.

Phase	Element	Important parameters	Unstandardized coefficients		Standardized coefficients			
			$b_i$	SE	Beta	t	p	R square
Gastric (G)	As	TC	0.19	0.003	0.999	59.08	<0.001	0.999
	Cd	AF	0.40	0.020	0.995	19.69	<0.001	0.990
	Co	TC	2.37	0.535	0.911	4.42	0.006	0.830
	Cu	TC	0.13	0.014	0.978	9.40	<0.001	0.957
	Fe	TC	1.28	0.208	0.951	6.13	0.002	0.904
	Ni	TC	0.04	0.004	0.985	11.38	<0.001	0.970
Gastrointestine (GI)	Pb	Clay	0.08	0.011	0.964	7.22	0.001	0.929
	As	TC	0.20	0.005	0.999	42.03	<0.001	0.999
	Cd	AF	0.27	0.049	0.940	5.52	0.003	0.940
	Co	TC	0.03	0.006	0.899	4.11	0.007	0.899
	Cu	TC	0.20	0.011	0.994	18.29	<0.001	0.994
	Fe	TC	93.22	8.695	0.983	10.72	<0.001	0.983
	Ni	TC	0.05	0.004	0.989	13.68	<0.001	0.989
	Pb	TC	0.39	0.058	0.959	6.75	0.001	0.959

Note:  $b_i$  = model's parameters (coefficients); SE = standard error; Beta = standardized model's parameters; t = t statistic; p = p value, R square = coefficient of determination, TC = total concentration; AF = available fraction.

variability of G, indicating that available fraction of Cd significantly contributed to bioaccessible Cd and can potentially be toxic to human beings (Yuan et al., 2011). Tang et al. (2018) found a strong positive correlation between bioaccessible Cd and sequentially extracted Cd exchangeable/acid soluble fraction of soil.

For Pb, just clay was included in SWLR and could explain 92.9% of variability of the G phase. This suggests that this element is accumulated in the smaller particle size fractions. The acid condition in the stomach is probably responsible for the adsorbed Pb from the clay surface making it more bioaccessible. Madrid et al. (2008) found a higher total and bio-accessible Pb concentration in the clay fraction (< 2 μm) as compared to coarser fractions in urban soils of Sevilla, Spain. Increased Pb bio-accessibility with decreasing particle size was also demonstrated by Cao et al. (2020). Metal bioaccessibility is influenced by the intrinsic properties of soil such as mineralogy, electrical conductivity (EC), pH, texture, and level of OM (Xing et al., 2019; Keshavarzifard et al., 2019). With regard to GI phase, only AF was included in SWLR for Cd and accounted 94% of variability. Also for As, Co, Cu, Fe, Ni and Pb, TC was included in SWLR and 99.9%, 89.9%, 99.4%, 98.3%, 98.9%, and 95.9% of variability of GI, respectively.

### 3.6. Human exposure assessment of PTEs via dust ingestion

The ADI, HQ, and CR values of PTEs calculated for adults through

**Table 4**

Carcinogenic and non-carcinogenic potential risks for individual PTEs based on total, gastric (stage I), and gastrointestinal (stage II) concentrations in fallout dust.

		As	Cd	Co	Cu	Fe	Ni	Pb
Total	$TDI_{oral}^a$	2.10E-03	1.00E-03	9.80E-02	1.40E-01	8.00E-01 <sup>b</sup>	1.70E-02 <sup>c</sup>	3.60E-03
	Oral RfD (mg kg <sup>-1</sup> )	3.00E-04	1.00E-03	3.00E-04	4.00E-02	7.00E-01	2.00E-02	3.50E-03
	$ADI_{ingestion}$	8.19E-06	3.71E-08	7.32E-05	1.69E-04	2.72E-01	7.09E-05	1.50E-06
Stage I	$ADI_{ingestion}$	1.60E-06	1.39E-08	2.21E-06	3.50E-05	6.90E-04	3.60E-06	5.04E-07
Stage II	$ADI_{ingestion}$	1.59E-06	2.11E-08	1.44E-06	2.27E-05	1.31E-04	3.08E-06	3.67E-07
<i>Non-carcinogenic risk</i>								
Total	$HQ_{ingestion}$	2.73E-02	3.71E-05	2.44E-01	4.23E-03	3.88E-01	3.55E-03	4.29E-04
Stage I	$HQ_{ingestion}$	5.33E-03	1.39E-05	7.38E-03	8.75E-04	9.85E-04	1.80E-04	1.44E-04
Stage II	$HQ_{ingestion}$	5.30E-03	2.11E-05	4.80E-03	5.68E-04	1.87E-04	1.54E-04	1.05E-04
<i>Carcinogenic risk</i>								
Total	Oral CSF (mg kg <sup>-1</sup> day <sup>-1</sup> )	1.50E+00	6.10E+00					1.50E+00
Stage I	$CR_{ingestio}$	1.23E-05	2.26E-07					2.25E-06
Stage II	$CR_{ingestio}$	2.40E-06	4.91E-08					7.56E-07
Stage II	$CR_{ingestio}$	2.39E-06	1.27E-07					5.50E-07

Note: Oral RfD = oral reference dose,  $ADI_{ingestion}$  = average daily intake via ingestion (μg kg<sup>-1</sup> day<sup>-1</sup>), HQ = hazard quotient, oral CFS = cancer slope factor-oral (mg kg<sup>-1</sup> day<sup>-1</sup>), and  $CR_{ingestio}$  = carcinogenic risk via ingestion.

<sup>a</sup> Baars et al. (2001),  $TDI_{oral}$  = Tolerable daily intake via ingestion (mg kg<sup>-1</sup> day<sup>-1</sup>) calculate for an adult weighting 70 kg.

<sup>b</sup> TDI for Fe (EFSA 2010).

<sup>c</sup> TDI for Ni (Food and Nutrition Board 2001).

#### 4. Conclusion

The present study characterized the nature of PTE (As, Cd, Co, Cu, Fe, Ni, and Pb) contaminants in fallout dust and suspended particulate matter in PM<sub>2.5</sub>, PM<sub>10</sub>, and TSP from an iron ore mining and industrial company in Iran. Both PM<sub>2.5</sub> and PM<sub>10</sub> in indoor and outdoor spaces exceeded the 24-h mean values of US National Ambient Air Quality Standard (NAAQS). Furthermore, the mean values of As, Cr, Co, Mn, and Ni in 3 PM size ranges surpassed the occupational/industrial and air quality guidelines. Despite higher mobility and oral bioaccessibility of Cd, this element showed the lowest risk assessment values due to its negligible concentration in fallout dust. Substantial amounts of PTEs (> 50%) are mainly associated with the more recalcitrant phase (residual) and, therefore, are much less available, mobile, and extractable in gastrointestinal solutions. Exposure index values (ADI, HQ, CR) for studied PTEs were all lower than the safe level and do not pose potential health hazard.

Accounting for oral bioaccessibility resulted in reduced health risk estimates as compared to the traditional approach of calculating hazard values (e.g., ADI, HQ, CR) using concentration data alone. Thus, oral bioaccessibility, as determined via the BARGE method, is recommended for future studies for more realistic estimates of uptake through oral exposure of contaminants such as PTEs. Further investigation is recommended to determine lung and dermal PTE bioaccessibility and to more reliably assess potential health risks through these pathways. The results of the present study provide direct evidence needed by GEG health, safety and environmental (HSE) managers to warn mine workers and other employees about the potential health risks caused by PTEs in dust. More broadly, this information is relevant to other mining operations worldwide.

#### CRediT authorship contribution statement

**Naghmeh Soltani:** Investigation, Writing - original draft preparation. **Behnam Keshavarzi:** Supervision, Conceptualization. **Farid Moore:** Writing - review & editing. **Mark Cave:** Writing - review & editing. **Armin Sorooshian:** Writing - review & editing. **Mohammad Reza Mahmoudi:** Formal analysis. **Mohammad Reza Ahmadi:** Industrial advising and logistical supporting. **Reza Golshani:** Investigation. All authors discussed the results and contributed to the final manuscript.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ecoenv.2021.111972](https://doi.org/10.1016/j.ecoenv.2021.111972).

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