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Health Risk Assessment of Heavy Metals in the Soil of Angouran Mineral Processing Complex in Iran

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ABSTRACT: This study aims at assessing the health-related risk of As, Co, Cr, Ni, and Cu in the soil around Angouran Mineral Processing Complex (AMPC), due to environmentally sensitive nature of the area, having agricultural activities, habitats of animal and plant species, and industrial activities integrated with each other. Soil samples have been collected from 74 points (0-20 cm) of the area and concentrations of heavy metals have been measured, using ICP-OES. The Geoaccumulation Index (Igeo), Enrichment Factor (EF), and Integrated Pollution Index (IPI) have been used to examine the pollution level. Moreover, hazard indices (HI), hazard quotient (HQ) and cancer risk (CR) have been utilized to assess the non-carcinogenic and carcinogenic health risks of heavy metals. The average concentration of heavy metals indicates that metals' concentration in the soil have increased in the following order: Cr = Ni> As> Cu> Co. Results from Igeo, Ef, and IPI show that As and Ni are placed in the very high pollution category. The non-carcinogenic risk of dermal absorption (adults = 1.30 E + 00, children = 1.35 E + 00) of Cr and Co polluted particles turn out to be very high. In addition, the risk of cancer as a result of the ingestion of As- and Cr-contaminated soil particles is high in both of age groups, with children being 68% more likely to be at risk of cancer than adults. Therefore, actions such as soil remediation should be done to reduce the risk of exposure and protect the health of the residents, especially the farmers.

Keywords: Cancer Risk, Hazard Indices, Hazard Quotient, Heavy Metal, soil.

INTRODUCTION

The intensity of human activities in recent decades have changed the nature's balance significantly (Petrosyan et al. 2019). Recent industrial development has resulted in a remarkable increase in pollution loads, imposed by toxicmetals, a significant environmental hazard for invertebrates, fish, and humans (Nasrabadi et al., 2015). Factories that concentrate and process heavy metals increase their levels in the soil. Exposure to heavy metals increases the possibility of health risks for the residents of the area. When heavy metals enter the human body, they damage the nervous system along with the enzymes, resulting in heart diseases, pregnancy, and cancer disorders (Davtalab nezam et al. 2016).

In recent years, the health risk assessment of carcinogenic and non-carcinogenic effect of heavy metals in

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human body has been done, using methods adopted by USEPA (US Environmental Protection Agency) in 2004. cancer risk (CR), hazard indices (HI), and hazard quotient (HQ) have been investigated by many researchers (e.g. Chonokhuu et al. 2019; Jamal et al. 2019; Eghbal et al., 2019; Aluko et al. 2018; Shakari et al. 2016; Karbassi et al., 2016; Xiao et al. 2017).

Health risk assessment process involves four steps, namely hazard identification, exposure assessment, toxicity (dose-response) assessment, and risk characterization. The first step (i.e. hazard identification) involves identifying the pollutants. The second step (i.e. exposure assessment) deals with measuring or estimating the severity, frequency, and duration of exposure to these pollutants. The third step focuses on the evaluation of the pollutants' toxicity. Cancer Slope Factor (CSF, a carcinogenic potency factor) and Response Dose (RfD, a non-carcinogenic threshold) are two important indicators of toxicity. The last step (i.e., risk characterization) predicts non-carcinogenic and carcinogenic health hazards of heavy metals for children and adults in order to obtain CR, HI, and HQ quantitative estimates (Kamunda et al., 2016).

Along with its zinc factory, Angouran Mineral Processing Complex (AMPC) includes lead and zinc concentration complexes and is located in Dandi Industrial Zone at Mahneshan, Zanjan Province, Iran. With a production capacity of over 23,000 tons per year, it is one of the largest producers of Iran, having a background of more than four decades of operation. It is located in the Angouran protected area, which is one of the oldest protected areas of Iran with a total area of 1,250 square kilometers. Almost 300 square kilometers of this area constitutes the Angouran wildlife refuge. Ghizil Ozen and Angouran Chay Rivers flow through the area, making it the home for dozens of aquatic bird species, seven amphibian species, and eight fish species. Many of the rare animals of Iran are found in this area. There are about 200 plant species in Angouran, as well. It is located in a protected area and expands metal industries. The main activities of its inhabitants are agriculture and animal husbandry. The area, under cultivation for agricultural and horticultural products in the city of Mahneshan comprises 11% of the total area of Zanjan Province. Moreover, a lion's share (81%) of this area is utilized for cultivating annual agricultural products, with the remaining 19%, being used for the cultivation of horticultural products. The accumulation of industrial, agricultural, and animal husbandry poles along with the habitats of different species in one area can potentially have some environmental problems that should be investigated (Shariati et al. 2011). This issue stems from the fact that the development of industrial activities, especially processing and concentrating units of heavy metals, increases the concentration of these metals in the soil and other environmental sources, exposing humans to them. These elements gradually accumulate in the soil due to their low mobility, and their entry into the food cycle and the environment causes problems for human health and other living organisms (Shariati et al. 2011; Miranzadeh et al. 2020). Studies by Shariati et al. (2011) showed that in Dandi industrial zone, the environment of the region was negatively affected by the accumulation of waste, left as cake on the margins of rivers and streams or open (mainly agricultural) lands. Being the waste from flotation and smelting of lead and zinc and concentrate production processes, this cake may have lost most of its lead and zinc from an industrial perspective. However, from an environmental point of view, it contains amounts of other potentially toxic elements including As, Cr, and Co that greatly exceed the allowable limits. Moreover, their study showed that waste or effluent pools were another major risk factor for the environment of the region. The agricultural soil of this area was affected by these contaminants and had major environmental anomalies. Considering the fact that, previous researches did not assess the health and contamination risk of potentially-hazardous metals in this area, the present study tries to firstly measure arsenic (As), nickel (Ni), chromium (Cr), cobalt (Co), and copper (Cu) concentrations and evaluate their contamination, using geoaccumulation index, Enrichment Factor, and integrated pollution index and secondly calculate their carcinogenic and non-carcinogenic risks to adults and children, using methods which are accepted by USEPA (US Environmental Protection Agency, 2004) in the soil around AMPC.

MATERIALS AND METHODS

AMPC includes lead and zinc concentration complexes along with its zinc factory. It is located in Dandei industrial zone, southwest of Zanjan province in Iran with the geographical coordinates of 47°40′37″ east and 36°34′20″ north. It is an impassable and mountainous area and the first geological studies on it were carried out by Bornell in 1960 (Gadimi & Nabatian, 2014). This area has been subjected to a metamorphic complex in the Microplate of Sanandaj-Sirjan in the Zagros orogenic belt, affected by Tertiary-Quaternary volcanic and geothermal activities in the Urmia-Dokhtar zone (Daliran& Borg, 2005). It is composed of present-day river alluvium in the central part and conglomerates and red tuffs in the northern one (Figure 1). About 15% of the area is irrigated and 70% of it, used as pastures. It has been one of the protected areas of the environment and has enabled tourism activities in order to preserve and restore plant and animal habitats for four decades until now.

The main winds of the Zanjan Province are Shareh winds. They blow from the southwest to the northeast, moving the humidity caused by the evaporation of the Mediterranean Sea, and making the air dry. Therefore, the region's dominant winds can be considered along the perpendicular direction of the basin, from the southwest to the northeast (Hosseini, 2014).

With respect to the study goals, the region’s vastness and characteristics, evaluation of the satellite images, the necessity of using the same sampling method in all points, the possibility of zoning and determining the pollution level, and preparing sufficient and proper samples whose results allow statistical analysis, this project employed a systematic sampling method, the center of which was AMPC. Moreover, the sampling stations were chosen in way that they could completely cover the agricultural lands and industrial areas in all directions around AMPC, as it was expected that the pollution would have more emission in the region, given AMPC’s activity for more than three decades. Therefore, a region with an area of 51 km^2 around the AMPC was chosen for sampling. At first, the sampling points were systematically chosen on the map. For this purpose, circles with a distance of 0.5 km were plotted, starting from AMPC, and some points on each of the circles were determined for the sampling. A total of 74 sampling stations were selected according to the study's goal, location of industrial areas, and area of the studied region. The sampling was conducted around the AMPC at first, and then with a distance of 1, 1.5, 2, 2.5, 3, 3.5, and 4 km. For this purpose, the 0-20-cm samples were taken after cleaning the sampling surface from both plants and roots and clods’ remains. Each sample was kept in a separate plastic bag, labeled in order to show the sample, itself, as well as the sampling point’s conditions. All these steps were part of the data quality provision goals, based on which the sampling plan was developed. The sampling at a distance of 3.5 and 4 km made the radius of pollution in the region more citable for interpretation. Moreover, some of these points were used as control samples to calculate the base concentration. Eventually, after sampling 500 to 700 gr from each station (if a sample mostly contained coarser grains, more amount of sample had to be taken), the samples in plastic bags were transferred to a laboratory. The sampling stage was finished by determining the location of the sampling point, using GPS.

Figure 1 depicts the sampling stations as well as the geographical location of the study area. After sampling, the samples got air-dried for analysis and their impurities, including gravels, clumps, organic materials, and plant root residues were taken away. Afterwards, they got dried in an oven (model: G601) at 105 °C for 24 hours. The samples were sieved through a 2 mm pore diameter polyethylene mesh and were returned to the laboratory (e.g. Jamal et al., 2019; Davtalab nezam et al. 2016; Ripin et al., 2014; Khodakarami et al., 2012). Soil properties related to mobility and bioavailability of heavy metals, including pH, soil texture, and soil organic matter (SOM), were selected for analysis. Soil pH was determined by preparing the saturated mulch extract based on the 1:2 soil/water ratio, using a pH meter analysis (pH meter model: MTT 65, made in Iran) (Klute, 1986). Moreover, soil texture was examined, using hydrometric method to determine the percentage of clay, silt, and sand (Gee & Bauder, 1986). Finally, SOM was measured, using the Black-Walley method in Soil Laboratory of Urmia University. Samples were sent to Zar Azma laboratory (located in Zanjan, Iran) to determine the total concentration of Cr, Co, As, Ni, and Cu, using Inductively Coupled Plasma-Optical Emission Spectrometry: ICP-OES (model: Perkin-Elmer ELAN 9000 made in US). In order to analyze the total concentration of heavy metals, the samples were digested, using the four-acid digestion method, including hydrofluoric, perchloric, nitric, and hydrochloric acid. For this purpose, each air-dried sample was weighted in a crucible and an amount of 5 ml concentrated nitric acid was added to it. It was kept at ambient temperature for 30 minutes. Then, it received 10 ml of perchloric and 2 ml of concentrated hydrofluoric acid. And placed on a heater, its temperature was increased to 100°C. Since this method's goal was to digest the solid sample completely, addition of hydrofluoric acid continued until the sample became transparent. In the end, it received 10 ml of concentrated hydrochloric acid and was kept at the same temperature for 10 minutes. Once it was cooled, it got transferred to a 50 to 100-ml volumetric flask, and was brought up to the volume, using double-distilled water. All chemicals used in this study were provided by the credible German Merck brand.

Statistical analysis of data and index calculations were carried out, using Excel 2013 and SPSS software (IBM SPSS Statistics 23) and the maps got prepared, using ArcMap 10 software. Analytical duplicates/replicates, standard reference material (OREAS 24b, and GBM908-10), and blank reagents (with an accuracy of 4% to 6%) were used for QA/QC. The detection limits for Cr, Co, As, Ni, and Cu were 1, 1, 0/5, and 1, respectively.

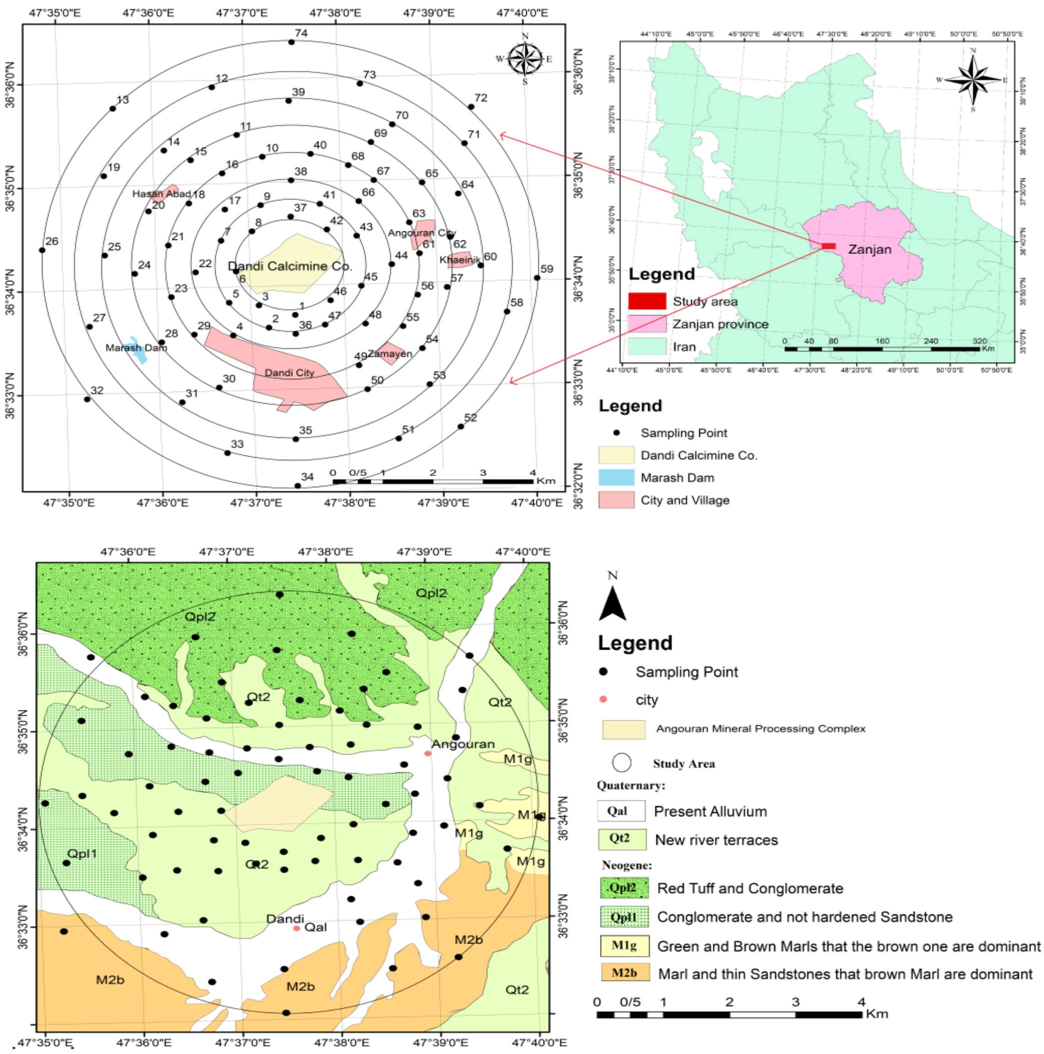

Fig. 1. The study area: the sampling stations and the geological map (Extracted from the 1/100000 geological maps of Mahneshan (Lotfi, 2011) and Takht-e-Soleiman (Babakhani & Ghulamash, 1991) with some changes)

Two important geochemical indices of Geo-Accumulation Index (Igeo), Enrichment Factor (Ef) and integrated pollution index (IPI) were used to assess the contamination of heavy metals (Nasrabadi et al., 2010). The Igeo index and its classification were introduced by Müller (1996) to compare the concentration of a metal before and after industrialization. The classification of this index and its calculation formula can be seen below (Equation 1), where C_n stands for metal's concentration in the soil and B_n, for the amount of metal in the reference sample. In this study, the average concentration of elements in the upper continental crust was considered as a reference (Dragović, et al. 2008; Badawy et al, 2016).

$$I_{geo} = \log_2 \left[C_n / (1.5 \times B_n) \right] \qquad (1)$$

0≥ Igeo unpolluted,

1> Igeo> 0 Unpolluted to medium pollution,

2> Igeo> 1 medium pollution,

3> Igeo> 2 medium to high pollution,

4> Igeo> 3 high pollution,

5> Igeo> 4 high to very high pollution, and

5< Igeo Very high pollution.

Having calculated each element at each site, IPI is calculated to assess the area's pollution by the PI_i average of elements (Equations 2 and 3).

$$IPI_i = \left(IP_1 + IP_2 + \ldots + IP_n\right) / n \quad (2)$$

$$PI_i = C_i / B_i \quad (3)$$

where n is the number of pollutants and PL_i, the pollution index of i^{th} heavy metals. C_i and B_i stand for the metal's concentration in the soil and in background, respectively. The IPI index is classified as follows (Chonokhuu et al., 2019):
IPI ≤1 for a low level of pollution,
1<IPI≤2 for a moderate level of pollution,
2<IPI≤5 for a high level of pollution, and
IPI > 5 for an extremely high level of pollution.

An element enrichment factor (*EF*) was initially developed to speculate on the origin of elements in the precipitation, or seawater (Duce et al., 1975; Zoller et al., 1974), but it was progressively extended to the study of soils, lake sediments, peat, tailings, and other environmental materials (Reimann and de Caritat, 2005). The formula to calculate *Ef* is:

$$\mathrm{Ef} = (C_i / C_{ie})_S / \left(C_i / C_{ie}\right)_{RS}$$

where C_i is the content of element i in the sample of interest or the selected background sample, and C_{ie}, the content of immobile element in the sample or the selected background sample (Zhang et al., 2007).

According to Sutherland (2000), five contamination categories are generally recognized on the basis of the enrichment factor:
EF<2, depletion to mineral enrichment;
2≤EF<5, moderate enrichment;
5≤EF<20, significant enrichment;
20≤EF<40, very high enrichment; and
EF>40, extremely high enrichment.

This study used the heavy metal health risk assessment method, introduced by the Environmental Protection Agency of the United States, US EPA. The risk assessment information system, introduced in the studies of Kamunda et al. (2016), Chonokhuu et al. (2019), Sun et al. (2020), and Shakeri & Yousefi (2016) helped providing the data, related to health risk assessment calculations.

The average daily dose (ADD) (mg / kg / day) of the three routes of exposure, namely ingestion, dermal absorption, and inhalation, is given in Equations 4 to 6.

Table 1 shows the exposure parameters used for the health risk assessment of Children (0-6 year) and Adults (6-70 year) (Chonokhuu et al., 2019).

$$ADD_{ing} = c \times R_{ing} \times CF \times ED \times EF / BW \times AT \quad (4)$$

$$ADD_{inh} = c \times R_{inh} \times EF \times ED / BW \times AT \times PEF \quad (5)$$

$$ADD_{derm} = c \times SA \times FE \times EF \times ABS \times ED \times AF \times CF / BW \times AT \quad (6)$$

Table 1. Values of different variables for the calculation of risk assessment

Parameter	Unit	Child	Adult
Body weight (BW)	Kg	15	70
Exposure frequency (EF)	days/year	350	350
Exposure duration (ED)	Years	6	30
Ingestion rate (Ring)	mg/day	200	100
Inhalation rate (Rinh)	m^3/day	10	20
Skin surface area (SA)	cm^2	2100	5800
Soil adherence factor (AF)	mg/cm^2	0.2	0.07
Dermal Absorption factor (ABS)	none	0.1	0.1
Dermal exposure ratio (FE)	none	0.6	0.6
Particulate emission factor (PEF)	m^3/kg	1.3×10^9	1.3×10^9
Conversion factor (CF)	kg/mg	10^{-6}	10^{-6}
Average time (AT):			
-For carcinogens	days	365×70	365×70
-For non-carcinogens		365×ED	365×ED

Hazard quotient (HQ) risk coefficient was used to estimate the health risk of ingestion, dermal absorption, and inhalation of soil particles. A dimensionless scale, it is calculated by dividing the Average Daily Intake (ADD) by the Reference Dose (RfD) of each heavy metal (Equation 7):

$$HQ = \frac{ADI}{RfD} \quad (7)$$

Classification of HQ values shows that if they are less than one, heavy metals will not have any adverse effects on health. However, HQ values, greater than 1, indicate negative effects on health.

Table 2 presents the Reference Doses (RfD) and Cancer Slope Factors (CSF) (Kamunda et al. 2016).

USEPA has introduced another index, called the Hazard Index (HI), in order to evaluate the non-carcinogenic effects. Equation 8 shows how to calculate this index.

$$HI = \sum_{k=1}^{n} HQ_k \quad (8)$$

where HQ_k shows the heavy metal's K value. According to HQ classification, HI values, below 1, indicate that there are no adverse health effects, while values, greater than 1, indicate a non-carcinogenic health risk for the exposed population.

Carcinogenesis is an increased risk of cancer during a person's lifetime as a result of exposure to carcinogens. The formula for the calculation of lifetime cancer risk is presented in Equation 9:

$$Risk_{pathway} = \sum_{k=1}^{n} ADI_k CSF_k \quad (9)$$

Risk is a unitless index. ADIk (mg / kg / day) and CSFk (mg / kg / day) are the average daily intake and slope factor for the K^{th} heavy metal. Finally, the risk of carcinogenicity is calculated by integrating the risks along the exposure routes, according to Equation 10.

$$\text{Risk(total)} = \text{Risk (ing)} + \text{Risk (inh)} + \text{Risk (dermal)} \quad (10)$$

where Risk (inh), Risk (ing) and Risk (dermal) stand for exposure through inhalation, ingestion, and dermal absorption of polluted particles, respectively. The Carcinogenic Risk (CR) classification shows that if CR< 10^{-6}, the risk of carcinogenicity will be negligible and if CR > 10^{-4}, the risk will be high. The CR values between these two values show moderate risk and are acceptable to some extent.

Table 2. Reference Doses (RfD) in (mg/kg-day) and Cancer Slope Factors (CSF)

Heavy Metal	Oral RfD	Inhalation RfD	Dermal RfD	Oral CSF	Dermal CSF	Inhalation CSF
As	3.00E-04	3.00E-04	3.00E-04	1.50E+00	1.50E+00	1.50E+01
Cr (VI)	3.00E-03	3.00E-05	6.00E-05	5.00E-01	-	4.10E+01
Co	2.00E-02	5.70E-06	5.70E-06	-	-	9.80E+00
Ni	2.00E-02	2.06E-02	5.60E-03	-	-	-
Cu	4.00E-02	4.02E-02	2.40E-02	-	-	-

RESULTS AND DISCUSSION

Table 3 gives the statistical results from soil samples' analysis as well as the global mean value of heavy metal concentrations. The average amount of sand in the study area 49.7%, being more than both silt and clay. Moreover, the average amount of silt was 34.3%. Finally, based on the results, the average amount of clay was 18.8% in the study area. Based on the soil texture triangle, proposed by the United States Department of Agriculture (USDA), this soil had the Loam texture. The percentage of clay in soil and SOM affect soil pH, which directly controls heavy metals' dissolution in the soil as well as plant growth (Dabiri et al., 2017). The range of SOM variations in soil samples was limited, ranging from 1.03% to 3.1%. As aforementioned, the amount of SOM affects the absorption of heavy metals due to the high cation exchange capacity. The average soil pH was 7.6, with the lowest and the highest pH values being 7 and 8.2, respectively. It indicated alkaline and slightly alkaline conditions and could indicate the presence of carbonate minerals such as calcite and dolomite in the region (Dabiri et al. 2017). It was also consistent with the presence of layers of marl in sedimentary rocks of the area. When the pH is alkaline and very alkaline, the cations are reduced in the soil solution. Therefore, increasing the pH is an effective factor to reduce the bioavailability of metal cations as well as the absence of any absorption by plant roots.

The mean of the central inclination of the data and the coefficient of the variation of a dimensionless criterion helped examining the distribution of statistical data. The mean value of the concentration of heavy metals indicated that the order of the increase in the concentration of metals in the soil was Cr = Ni> As> Cu> Co. The highest amount, the lowest amount, and the average amount of Cr in the region were 115, 32, and 70.8 ppm, respectively. Cr displayed a 68.5% increase in comparison with World Mean Soil (W.MS). The highest amount, the lowest amount, and the average amount of Ni in the samples were 280, 30, and 70.7 ppm, respectively, which increased by 292.7%, compared to W.MS. As showed a higher increase than other metals, based on W.MS. The average amounts of other metals were also higher than W.MS, indicating some danger in the region. The highest coefficient of variation was 79.5% for Co, showing the intensity of Co changes. Similar to Co, the coefficient of As variation was higher than other metals. Cr had the lowest coefficient of variation (25.7%).

Table 3. Descriptive statistics for soil samples' results (element as ppm and SOM, clay, silt, and sand as percentage)

	Min	Max	Average	Coefficient of variation (%)	W.MS *
As	12.1	100	34.09	65.1	4.7
Co	7	92	14.8	79.5	6.9
Cr	32	115	70.8	25.7	42
Ni	30	280	70.7	50.3	18
Cu	14	84	32.4	43.7	14
pH	7	8.2	7.6	3.8	-
SOM	1.03	3.1	1.9	29	-
Clay	10.1	42.2	18.8	51	-
Silt	17.2	70.4	34.3	35.2	-
Sand	6.1	72.8	49.7	38.7	-

*(Shakeri & Yousafi, 2016)

Table 4 presents the results from Igeo calculation. According to the index, the increase in heavy metal pollution was as follows: As> Ni> Cr> Cu> Co. As (with a mean value of 3.6) fell into the high pollution category. Moreover, the majority (82%) of the samples fell under high pollution category, while the others belonged to moderate one. The highest, the lowest, and the average amounts of Ni were 3.3, 0, and 1.1, respectively. Therefore, it belonged to moderate pollution category. High pollution of Ni was found in 4% of samples and more than 95% of the samples belonged to moderate pollution category. The highest, the lowest, and the average Igeo amounts of Cr were 1.1, -0.7, and 0.3, respectively, showing that 85% of the samples fell under moderate pollution category, and 15%

under unpolluted one. Similar to Cr, the highest, the lowest, and the average amounts of Cu were 1/1, 1/4, and -0.3 respectively, puting it in unpolluted to moderate pollution category. Moderate pollution was observed in 21% of the samples. Co had the lowest pollution level and only 3% of the samples belonged to moderate pollution category.

The calculated values for Ef index for As, Cr, Co, Cu, and Ni were 7.3, 0.1, 0.1, 0.1, and 0.3, repsectively. Similar to the results obtained from Igeo, As showed the highest amount and highest enrichment. High enrichment of As was seen in 14% of samples in the region. For 3% of the samples, Ni showed moderate enrichment.

Figure 2 illustrates the spatial variation map of the IPIi index, using ordinary kriging (RMS = 1.5). As (IPI average=21.3) and then Ni (IPI average=3.9) contributed the most for the increase in this index. On the other hand, Cr (IPI average=1.6), Co (IPI average=0.8), and Cu (IPI average=2.3) had smaller impacts on this index's changes. Based on the spatial distribution map of the index, a total of 15 square kilometers of the study area, including its northern and southeastern areas, fell under moderate pollution category and the other areas with a two-kilometer distance from the AMPC belonged to high pollution and very high pollution categories.

Non-carcinogenic risk of heavy metals for children and adults was calculated based on RfD and ADI values. Table 5 presents the ADI values for non-carcinogenic effects, while Figure 3 demonstrates the results of HQ calculation.

Table 4. Results of Igeo and Ef index

	Igeo			EF		
	Min	Max	Average	Min	Max	Average
As	2.3	5.3	3.6	1.1	12.0	3.7
Co	-1.8	1.8	-0.9	0.07	0.6	0.1
Cr	-0.7	1.1	0.3	0.06	0.1	0.1
Ni	0	3.3	1.1	0.1	1.1	0.3
Cu	-1.4	1.1	-0.3	0.05	0.3	0.1

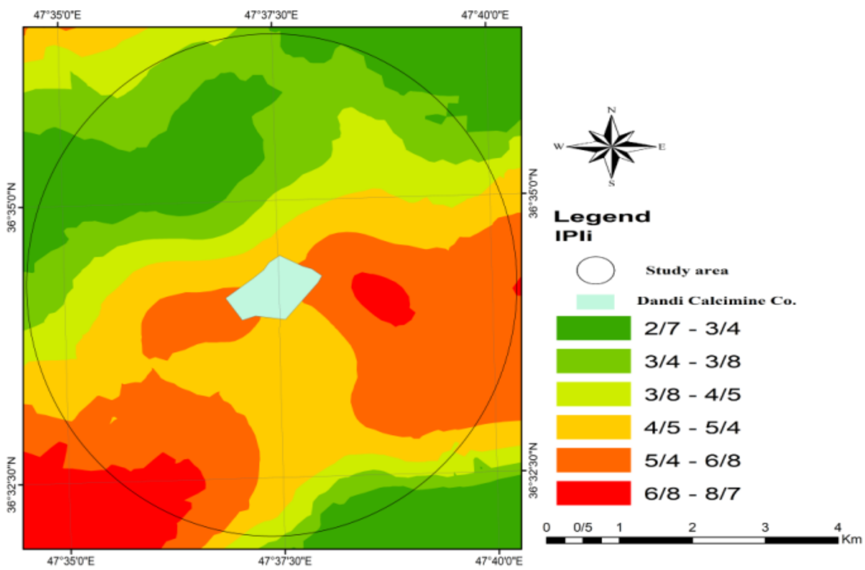

Fig. 2. Spatial distribution of IPIi index in the study area

As aforementioned, both HQ and HI values, being less than 1, do not indicate a health risk. However, values greater than 1 indicate non-carcinogenic health risk. In regard to all of the three exposure routes, the HI values were 1.50E + 00 and 1.74E + 00 for adults and children, respectively. These values show non-carcinogenic health risk. For adults, the risk of dermal absorption (1.30E + 00) was greater than the risk of ingestion (1.95E-01) and for children, the risk of dermal absorption (1.35E+00) was greater than the risk of ingestion (3.90E-01). Non-carcinogenic risk from inhalation of contaminated soil particles was at the lowest level for both age groups.

Table 5. Non-carcinogenic Average Daily Intake (ADI) Values (mg/kg/day)

Receptor		**Heavy metals**				
	Pathway	**As**	**Cr**	**Co**	**Cu**	**Ni**
Adult	Ingestion	4.67086E-05	9.70381E-06	2.03073E-05	4.44835E-05	9.69086E-05
	Inhalation	7.18594E-09	1.49E-08	3.12E-09	6.84E-09	1.49E-08
	Dermal	1.13782E-05	2.36E-05	4.95E-06	1.08E-05	2.36E-05
Child	Ingestion	9.34173E-05	1.94E-04	4.06E-05	8.9E-05	1.94E-04
	Inhalation	3.59E-09	7.46E-09	1.56E-09	3.42E-09	7.45E-09
	Dermal	1.18E-05	2.45E-05	5.12E-06	1.12E-05	2.44E-05

Exposure to metals can occur through direct contact of the skin with metal surfaces and other solid or powder materials that contain them. Moreover, it may take place as a result of deposition of particles, containing metal in the air (Schaeider & Kildes, 1999). The dose or amount of deposited metals on the skin may penetrate its inner layers. The dose and fate of heavy metals on the skin are determined according to contact characteristics and physiological properties of the skin. These properties include pH, temperature, and presence of salt, amino acids, and proteins and lipids on the skin surface that can be dissolved (Taylor & Machado-Moreira, 2013). After exposure to metals, they may be washed or scraped off either the skin surface air (Schaeider & Kildes, 1999), the horny layer of skin (14 days), or the epidermis (47 days) (Berfstresser & Richard, 1977), based on the amount of metals that penetrate the skin.

Considering the calculation of non-carcinogenic risk, among the heavy metals, Co (Mean=8.69E-01) and Cr (Mean=4.27E-01) entailed higher risk to adults, in comparison with other metals. Similarly, for children, Co (Mean= 9.00E-01) and Cr (Mean=4.73E-01) posed a higher risk. The non-carcinogenic risk of Co and Cr stems from dermal absorption. In general, children are more sensitive to non-carcinogenic health risk, and dermal contact and ingestion of contaminated soil with Cr and Co can cause them some health problems. As poses a higher ingestion health risk in comparison with the other metals, with children facing 51% higher risk than adults, due to their lower body surface area and their higher possibility of ingestion. These results are in line with the results of the studies by Jamal et al. (2019) and Fan and Wang (2017).

Soil contamination with Co often occurs in areas close to industrial plants and factories. Measurement of Co levels at the target organ level is often performed in the workplace, where the skin and respiratory system are the primary target organs of Co toxicity. Co mobility in the soil is low. Research shows that usually Co remains up to 5 cm under the ground and 95% of its deposited amount remains inactive. Increased acidity and anaerobic conditions mobilize Co. Although cobalt plays an important role as a constituent of vitamin B12, over-exposure to it has negative health effects. Systemic health effects that result from a complex clinical syndrome mainly involve nervous system problems (e.g. hearing and visual impairment) not to mention cardiovascular and endocrine problems (Fujikawa & Fukui, 2001).

Table 6 and Figure 4 show the carcinogenic risk in terms of daily intake of heavy metals throughout the life span. Considering the fact that, there were not any CSF values for Ni and Cu and some exposure pathways for Co and Cr, the lifetime carcinogenic risk was not calculated for them. Results from calculation of total cancer risk showed that children face 61% higher risk of cancer than adults. Soil samples were classified as moderate to unsatisfactory in terms of carcinogenic risk classification for children and adults. Among the heavy metals, considering all three exposure routes for adults, As (3.73877E-05), Cr (2.11E-05), and Co (1.31216E-08) displayed high, moderate, and low risk, respectively. The same was true for children, i.e., the calculated risk of As (5.75853E-05) was higher than Cr (3.89E-05) and Co (6.12343E-09). The study by Nasrabadi et al. (2013) showed that As was classified as carcinogenic. The study by Engwa et al. (2019), which was conducted on carcinogenicity of As and Cr, showed that the carcinogenic mechanism of As in the body involved epigenetic changes, damage to the DNA storage system, and reactive oxygen species. Changes in histones, DNA methylation, and microRNAs are important epigenetic changes, caused by As. Potentially they can induce malignant cell growth. Moreover, skin, prostate, and lung cancers are also associated with As poisoning. In addition to As, Cr poisoning may cause cancerous tumors too, due to DNA damage.

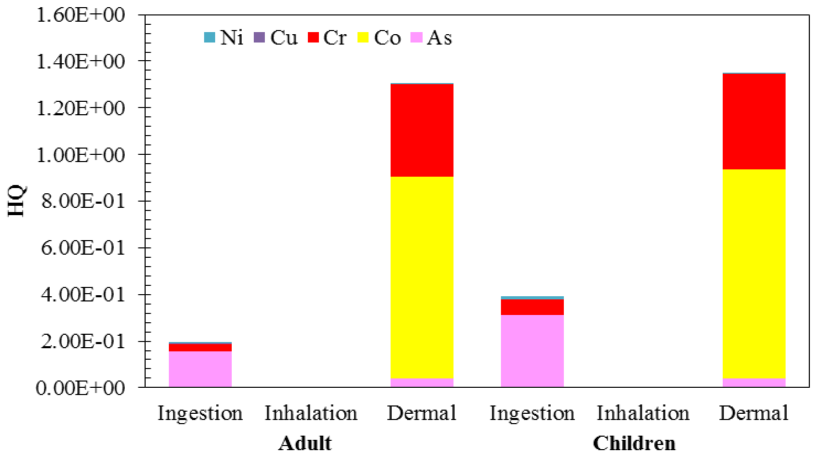

Fig. 3. Hazard quotient (HQ) values

Table 6. carcinogenic Average Daily Intake (ADI) Values (mg/kg/day)

Receptor		Heavy metals		
	Pathway	**As**	**Cr**	**Co**
Adult	Ingestion	2.0018E-05	4.15878E-05	
	Inhalation	3.07969E-09	6.39812E-09	1.33894E-09
	Dermal	4.87638E-06		
Child	Ingestion	3.73669E-05	7.76305E-05	
	Inhalation	1.43719E-09	6.2484E-10	2.98579E-09
	Dermal	1.00891E-06		

In both age groups, ingestion (adults = 5.08209 E-05 and children = 9.48656E-05) was the main route of exposure, posing a higher risk. Therefore, in general, ingestion of soil, contaminated with Cr and As, poses a very high carcinogenic risk.

Table 7 provides sampling points with high concentrations of metals, which fell under highly polluted category, based on pollution indices, showing high probability of pollution on the basis of CR. The table also presents their geographical coordinates as representative for the entire region. As it is clear from the table, points in the very high pollution category are distributed in the area around AMPC. Moreover, the sampling stations in the wheat fields and agricultural fields face a high risk and need serious attention.

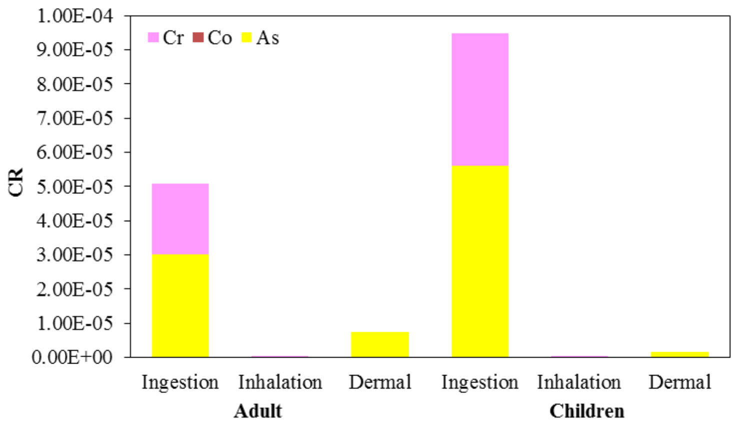

Fig. 4. Cancer Risk values for adults and children

Table 7. Introduction of heavy metal contaminated sampling stations, pollution classification, and carcinogenicity

Number	UTM geographical coordinates		Concentration (ppm)					Pollution classification	Cancer Risk (Total)		Land Use
	X	Y	As	Cr	Co	Ni	Cu		Adults	Children	
4	734292	4049654	61.9	69	11	42	17	V.H	M	V.H	
6	733927	4050261	48.5	53	10	30	14	V.H	M	M	Fuel storage location
23	732895	4049801	100	87	43	123	33	V.H	M	V.H	Sandy areas
43	735850	4050988	57.1	79	18	100	55	V.H	M	M	Wheat fields
44	736412	4050390	100	103	92	280	71	V.H	M	V.H	Areas around the AMPC
53	737018	4048248	100	88	63	211	48	V.H	M	V.H	-
54	736901	4048892	100	84	29	123	37	V.H	M	V.H	Agricultural land
56	736825	4049846	100	67	21	97	46	V.H	M	V.H	Wasteland
57	737294	4049983	43.9	63	14	75	38	V.H	M	M	Wasteland
61	736854	4050587	100	73	19	88	33	V.H	M	V.H	

Very High :V.H; Moderate :M

CONCLUSION

This study was carried out to investigate the carcinogenic and non-carcinogenic health risks of Co, As, Cr, Cu, and Ni metals in the soil around AMPC, which includes lead and zinc concentration complexes as well as a zinc production factory. This area was selected due to the fact that it is environmentally sensitive. Moreover, in addition to industrial activities, including the concentration and processing of heavy metals, it is used for agricultural activities, pastures, and animal husbandry. Lastly, it is the habitat for various and rare animal and plant species.

Texture analysis of soil samples showed that the percentage of sand was higher than silt and clay in the area. Hence, it was possible that plants easily accessed soil solution and absorbed heavy metals. Therefore, other properties that affect absorption of heavy metals from soil, including pH and SOM, were investigated, too.

Although the area under study involved mostly agricultural and pasture land, SOM content of the soil was insignificant, indicating the residual effect of smelting factories and heavy metal concentration in the area's soil. The range of pH changes also showed alkaline to slightly alkaline soil conditions due to the presence of marl layers in the sedimentary rocks of the area and the presence of carbonate minerals in the area. The heavy metal concentration in the region increased in the following order: Cr = Ni> As> Cu> Co. High coefficients of As and Co variation showed the effect of anthropogenic activities on their distribution in the region. Moreover, examining As concentration in the samples showed that, according to Iranian standard, they were in an undesirable condition. Calculation of Igeo, EF, and IPI indices showed that As and Ni were at the highest level of pollution. The spatial distribution map of the IPI index showed that the areas around AMPC fell under highly polluted category. This issue stemmed from the fact that, in addition to the waste cake, the passing of vehicles and transportation of minerals and waste increased its concentration in the soil surface. The status of the samples in terms of non-carcinogenic health risk of dermal absorption of Cr and Co contaminated soil particles was extremely dangerous for both age groups. These findings are very important for the residents, especially the farmers who are in direct contact with the soil. It necessitates precautions such as wearing gloves and masks. Furthermore, results from evaluation of heavy metal carcinogenic risk index for both age groups showed that ingestion of soil, contaminated with As and Cr, was the main cause of exposure, increasing the possibility of cancer.

In developing countries, there are very few studies which have examined exposure to heavy metals. The potential non-carcinogenic and carcinogenic risks of heavy metals around AMPC indicate that the region requires integrated studies on all exposure sources (i.e., air, water, and food). Moreover, considering the fact that the study area is an agricultural one, the carcinogenic risk increases for adults. This is due to the fact that farmers undergo ingestion of soli particles, sticking to their hands, dermal exposure during farm work hours, and inhalation of polluted soil and dust, thus they face a higher risk. Finally, based on the results in regard to the high concentrations of toxic metal around AMPC, their remediation is particularly necessary to maintain the health of the vulnerable population.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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