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Health risk assessment associated with heavy metals through fractioned dust from coal and chromite mines in Pakistan

Zakia Sultana · Muhammad Yasir Abdur Rehman · Hudda Khaleeq Khan · Riffat Naseem Malik

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Abstract Heavy metals exposure through dust emissions pose a health risk to workers in coal and chromite mines. The processes involved in mining are noteworthy for the generation of heavy metalcontaminated dust which causes human health implications, especially to the workers that are mainly exposed to such toxins. This study determined pollution levels in coal and chromite mines and calculated the health risk of workers being exposed to heavy metal-contaminated dust. We used fractioned dust with particle sizes < 75, 75–106, and 107–150 µm to assess the pollution levels, anthropogenic impacts, geo-accumulation index, and enrichment factor for selected coal and chromite mines. Through a probabilistic approach, Monte Carlo simulations were used to determine health risks. The findings revealed that the smallest size dust fraction ($<75 \mu m$) contained the highest metal concentrations. Ingestion was considered a prominent exposure route contributing

Zakia Sultana and Muhammad Yasir Abdur Rehman have contributed equally to this manuscript.

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Z. Sultana · M. Y. A. Rehman · H. K. Khan · R. N. Malik (⊠) Environmental Health Laboratory, Department of Environmental Sciences, Quaid-i-Azam University, Islamabad, Pakistan e-mail: r_n_malik@qau.edu.pk to health risk. In the dust fraction ($<75 \mu m$), chromite mines exhibited the highest Cr (340.6 mg/kg) and lowest Cd (8.4 mg/kg) concentrations. In coal mines, Mn (284.9 mg/kg) and Cd (2.1 mg/kg) were measured highest and lowest, respectively. Pollution assessment revealed dust to be moderately polluted. Health risk assessment showed that Cr in chromite mines exhibited a mean HI value of 1.16E + 00 that was higher than the safe level (HI > 1) having the potential to cause significant health risk to workers. In coal mines, the estimated total HI was 6E-1. Sensitivity analysis revealed concentration and exposure time to be the most influential parameters contributing to risk. Therefore, governmental and nongovernmental organizations must develop dust pollution control guidelines and mitigation measures to safeguard the health of mineworkers by limiting heavy metal exposure.

Abbreviations

EF	Enrichment factor
ADD	Average daily dose
CR	Cancer risk
Igeo	Geo-accumulation index
HI	Hazard index
HQ	Hazard quotient
USEPA	United States Environmental Protection
	Agency

HMs Heavy metals RfD Reference dose

Introduction

Heavy metals are found in nature, and a few of them also known as essential heavy metals such as Cu, Fe, Zn, and others are needed for the survival of living organisms at low concentrations, but severe harm (cancer-causing, coronary, nervous, sexual, and other) may occur if their presence exceeds natural levels (Jaishankar et al., 2014). However, nonessential heavy metals, on the other hand, can be harmful to living beings even at low concentrations. They can get into humans through the air, water, soil, and plants (Gautam et al., 2016). The risk caused by heavy metal exposure to human well-being continues to be a serious concern because of their pervasiveness in the environment (Tchounwou et al., 2012). Individuals, particularly in occupational settings, are more likely to be exposed to them frequently. A considerable volume of literature has also been stated on the occurrence of heavy metals in different occupational settings such as battery manufacturing workshops (Shen et al., 2021; Singh et al., 2013), recycling units for e-waste (Leung et al., 2008; Singh et al., 2018), and mechanical workshops (Sabouhi et al., 2020).

Despite its enormous importance in socioeconomic growth, mining is one of the most significant occupational settings that contribute to heavy metal pollution. Despite the fact that many other activities contribute to heavy metal emissions in the environment, mining operations are notable for releasing a huge quantity of particles. Furthermore, the toxicity of contaminants associated with such emissions is higher (Trechera et al., 2021). Drilling, blasting, loading, unloading, and transporting materials are all examples of mining operations that can release dust-bound heavy metals in a variety of sizes (Gautam et al., 2016). While considering mining activities, a large amount of metalliferous dust is generated which is among the leading causes of adverse health effects in humans (Csavina et al., 2012). Dust serves as a carrier for a large number of pollutants (Tong et al., 2019), and the size of a dust particle is critical in determining the risk to human health (Csavina et al., 2012; Shen et al., 2021). Since different size fractions of dust have varying concentrations and accumulations of trace elements (Lanzerstorfer, 2017), fine dust particles tend to penetrate deep into the lungs transporting the contaminants directly into the blood as compared to the coarser particles that settle in the upper respiratory tract (Valiulis et al., 2008).

The evaluation of health risks is a critical approach to assess significant risks caused by toxic pollutants when they come in contact with the human body (Pan et al., 2016). The findings can aid in the development of worker safety measures that mostly lack in developing countries. The concentration of heavy metals and the exposure pathway parameters are important in estimating human health risks (Du et al., 2019). The two most common approaches for assessing health risks are deterministic and probabilistic risk assessment. The traditionally used deterministic method obtains the output risk by adopting a mean or maximum concentration value that may result in providing incomplete health risk information (Tong et al., 2019). There are numerous uncertainties in the process of assessing health risks because parameters such as body mass index (BMI), exposure period, pollutant concentration, and others can vary so significantly that a single mean estimate is often unreliable (Rajasekhar et al., 2020). To overcome these uncertainties, probabilistic method is used which is a statistical method that makes use of probability distribution providing more realistic and reliable results (Tong et al., 2019).

Coal and chromite are the top-ranked mineral resources of Pakistan in terms of their vast extraction and consumption. Worldwide coal is the second most used energy source, and in coming decades, its consumption may increase, most likely due to its increased demand and extraction by the Asiatic Pacific region (Trechera et al., 2021). Pakistan's coal reserves are substantial, and it is a comparatively cheaper source of energy than any other source (Raza & Shah, 2020). Pakistan ranks 7th in owning lignite coal reserves which fulfil Pakistan's current need for energy consumption (Malkani, 2015). Chromite mines are a large reservoir for chromium production which is one of the essential metals used in metallurgical and refractory industries. The metallurgical industry processes about 90% of the chromite extracted for the manufacture of stainless and alloyed steel, as well as nonferrous alloys (Bachmann et al., 2019). Pakistan ranks 12th in the worlds' chromite production (Malkani, 2015). Occupational hazards caused by heavy metal pollution are a problem concerned on a global level, particularly in developing countries (Okonkwo et al., 2021).

In Pakistan, there has been limited research on the health risks associated with heavy metals in occupational settings. For instance, studies were conducted on possible risks of heavy metals to human health from leather industries (Junaid et al., 2017), industries that make surgical instruments (Junaid et al., 2016), marble industries (Noreen et al., 2019), battery recycling, and welding workshops (Baloch et al., 2020). Moreover, these studies focused on a single pathway to assess the health risk or used either deterministic or probabilistic methods to evaluate the health risk. However, studies on the health risk of dust-bound heavy metals in the mining sector of Pakistan are lacking. Literature showed that there is only one study that investigated heavy metals content in coal dust with a focus on overall potential risks in the surrounding population (Ishtiaq et al., 2018), while other studies were mainly focused on evaluating possible health risks of heavy metals in other matrices (soil, plant, and water) (Nawab et al., 2016). Occupational risk assessment of dust-bound heavy metals in coal and chromite mines was thus needed to discern the subsequent effects on worker's health. Furthermore, one of the sustainable development goals is to promote healthy and stable working conditions for all workforces. To our knowledge, no studies have been performed in coal and chromite mines of Pakistan to address occupational health risks associated with dustbound heavy metals. This is the first comprehensive study to assess the health risks posed by dust exposure to coal and chromite mine workers. The objectives of the current study were to assess the enrichment and pollution levels of heavy metals (HMs) in the dust of coal and chromite mines, and to assess the occupational health risks associated with dust HMs through ingestion, inhalation, and dermal pathways, and to use a probabilistic model to measure the contribution of different exposure parameters in health risk assessment.

Materials and methods

Study area

The current study was carried out in coal and chromite mines located in the province of Punjab and Balochistan, Pakistan. Coal and chromite are the top-ranked mineral resources of Pakistan in terms of their vast extraction and consumption. The chromite mines studied are located in Muslim Bagh, district Qilla Saifullah, and the coal mines studied are located in Khushab, Makarwal, and Quetta. The location map is shown in Fig. 1.

Sampling and sample pretreatment

A total of 24 composite samples (14 from coal mines, 5 from chromite mines, and 5 from chromite ore processing plants) were taken. Mines dust samples were collected from the hardened ground at no fewer than five sub-sites at each sampling site (Men et al., 2018). The weight of each sample was around 40 g. Each sample was obtained by sweeping a $4-10 \text{ m}^2$ area gently with a clean plastic brush and tray. Afterward, the sample was transferred to airtight polyethylene packs for storage. Each sampling point is located within 1 km of the mining area and processing plant. Each sample was taken with clean plastic utensils (brush and dustpan) by delicately sweeping an area, and afterward, the sample was transferred to airtight polyethylene packs for storage. After that, all of the samples were labeled, sealed, and transported to the Environmental Health Laboratory, Department of Environmental Sciences, Quaid-i-Azam University (Islamabad, Pakistan), where they were stored at room temperature. After that, large particles were manually collected from the sample bags before further procedure. Then using a mechanical sieve shaker, the whole mass of dust was sieved. Dust samples were subjected to shaking for 30 min with mechanical shaking into the following size fractions: $<75 \mu m$, 75-106 µm, and 107-150 µm, known to be widely found in resuspended dust and soil grain and could be easily segregated using a combination of sieves (Souli et al., 2009). Subsamples obtained were then subjected to chemical analysis.

Chemical analysis

Heavy metals, i.e., Cd, Zn, Cu, Mn, Pb, Cr, Ni, and Co were selected based on their wide occurrence and toxicity. Acid digestion of dust samples was carried out as described previously (Ehi-Eromosele et al., 2012). In summary, a Kjeldahl flask was filled with 1 g of dried and homogenized dust sample. Fresh aqua regia was prepared by mixing HCl and



Fig. 1 Study area map. a, c Sampling locations for coal mines in province Punjab and Balochistan and b sampling locations for chromite mines in province Balochistan

 HNO_3 in the ratio of 1: 3. The flask was then filled with 12 mL of aqua regia and kept on the hotplate for two hours at 110 °C. During the heating process, the flasks were capped with a watch glass. After digestion was done, the flasks were taken off the hotplate and left to cool down. When the liquid in the flask reached room temperature, it was filtered into a 50-mL volumetric flask using filter paper (Whatman No.42). To make the volume 50 mL, deionized water was used. For accuracy of the overall experiment, blank solutions were also prepared parallel with original samples; usually, after every 15 samples, one blank solution was prepared. Following proper calibration of the instrument with standard solutions, the concentrations of heavy metals in the samples were determined using an atomic absorption spectrophotometer coupled with a graphite furnace (PerkinElmer, AAS-700).

Quality control and quality assurance (QC/QA)

Strict quality assurance and quality control protocols were applied throughout sampling and laboratory analysis. Containers and glassware were submerged in HNO_3 (10%) overnight, washed by distilled water, and oven-dried before use. Chemicals and reagents of analytical grade were utilized. To minimize partialities, reagent blanks and triplicate samples were analyzed for quality assurance (QA) of analytical methods. The spiking method was used to validate the analytical method utilized. This was accomplished by assessing the metal concentrations of non-spiked and spiked dust samples in duplicate (Naz et al., 2018). For spiking, 1 mL of different concentrations of the standard was introduced to 1 g of dust sample, which was then digested. The following formula was used to measure the percent recoveries:

$$\% \text{Recovery} = \frac{s - y}{z} \times 100$$

's' shows spiked sample's metal concentration, y is un-spiked sample's metal concentration, and z is spiking concentration measured in mg/L. The average recoveries for all metals ranged from $92.4 \pm 1.2\%$ to $97.8 \pm 1.8\%$. The experimental samples and the blank solution were prepared in the same way. The calibration curves prepared from each metal standard yielded good linearity.

Pollution assessment

The geo-accumulation index and the enrichment factor have been assessed to identify heavy metals contamination levels in the mines. Their efficiency in the assessment of pollution levels has been reported earlier (Pathak et al., 2015). Our study area lacks background data in soils due to which background reference values used were the shale values of examined heavy metals. The average shale values (mg/kg) for Cd, Fe, Co, Cr, Cu, Mn, Ni, Pb, and Zn were 0.30, 47200, 19, 90, 45, 850, 68, 20, and 95, respectively (Turekian & Wedepohl, 1961). The indices that were used are described below:

Enrichment factors (EF)

To calculate the contribution of human origin, the strength of heavy metal enrichment was determined using the enrichment factor (Nweke & Ukpai, 2016). The following equation is used to measure it (1).

$$EF = \frac{\left(\frac{Cn}{Cref}\right)sample}{\left(\frac{Bn}{Bref}\right)background}$$
(1)

In the above equation (Cn/Cref), sample shows the ratio of concentrations of the analyzed metal in the sample, whereas (Bn/Bref) background shows the ratio of concentrations of analyzed metal in the background. Since iron (Fe) concentrations are less variable, and it is present in large concentrations in mines studied, hence it was used as a normalization factor (Christophoridis et al., 2019).

Geo-accumulation index

Geo-accumulation index has been proposed for the first time by (Muller, 1969). It is useful in determining the extent of contamination in soils or sediments that are polluted by harmful metals. It is calculated using Eq. (2).

$$Igeo = log2\left(\frac{Cn}{1.5 \bullet Bn}\right) \tag{2}$$

where Cn is the estimated heavy metal concentration in the soil and Bn is the geochemical background value. To normalize the possible variations in the baseline data, a constant of 1.5 is added (Christophoridis et al., 2019). There are several classes in the geo-accumulation table, of which the largest class signifies greater enrichment (Li et al., 2014). The categorization of classes is stated in Table S1 (Supplementary material).

Health risk assessment

Human health risk assessment, according to the (USEPA, 2014), is a tool for assessing the degree and likelihood of negative health impacts in people who are exposed to toxic substances in contaminated environmental media. Dust was divided into three size fractions, i.e., <75 μ m, 75–106 μ m, and 107–150 μ m. Heavy metal concentrations in these dust fractions were compared. Dust with size fraction <75 μ m was further analyzed for toxicity and health risk assessment as it is well known that particles smaller than 100 μ m are quickly resuspended and stick to the skin, while particles that are even smaller than 63 μ m can effectively adhere and become an effective means of transport for trace elements (Botsou et al., 2020).

Average daily intake

To evaluate human risks, the USEPA guidelines for exposure assessment were used in this study (USEPA, 1989, 1997, 2001). To measure the exposure of each metal through different pathways, average daily dose (ADD, mg/kg/day) was assessed particularly for highly exposed on-site workers using Eqs. (3), (4), and (5) (Sabouhi et al., 2020).

Ingestion: (ADD_{ing}, mg/kg/day)

$$ADDing = \frac{C_{dust.} IngR.EF.ED.10^{-6}}{BW.AT}$$
(3)

Inhalation: (ADD_{inh}, mg/kg/day)

$$ADDinh = \frac{C_{dust.}InhR.EF.ED}{PEF.BW.AT}$$
(4)

Dermal interaction (ADD_{dermal}, mg/kg/day)

$$ADDdermal = \frac{C_{dust.}SA.AF.ABS.EF.ED10^{-6}}{BW.AT}$$
(5)

The exposure scenario's standard values were adapted from US Environmental Protection Agency (USEPA, 2014) published manuals stated in Table S2.

Noncarcinogenic health risk

Hazard quotient (HQ) and hazard index (HI) were used to calculate the noncarcinogenic risk of heavy metals. Heavy metals' noncarcinogenic health risk was quantified using the hazard quotient and HI. The noncarcinogenic risk by inhalation (HQ_{inh}), ingestion (HQ_{ing}), and dermal absorption (HQ_{dermal}) was determined by taking the ratio of the average daily dose (ADD) of the heavy metals to their respected reference doses (RfD) used for equivalent pathways using Eqs. (6), (7), and (8). The calculations were performed according to the published protocol of USEPA (USEPA, 2007).

$$HQing = \frac{ADDing}{RfDo}$$
(6)

$$HQinh = \frac{ADDinh}{RfDi}$$
(7)

$$HQdermal = \frac{ADDdermal}{RfDdermal}$$
(8)

The maximum allowable dose of a toxic substance to the human body that is most likely to cause no negative consequences throughout a lifetime is referred to as a reference dose. The average daily dose of a certain substance is referred to as ADD. The abbreviations ADD (ing, inh, and dermal) stand for average daily dose through ingestion, inhalation, and dermal contact, respectively. RfD_o is the reference dose through the ingestion path, RfD_i is the reference dose via inhalation path, and RfD_{dermal} reference dose through dermal absorption. Its unit is mg/kg/day. If the estimated HQ is less than 1, no negative health implications are expected while HQ value greater than 1, which means that the findings have the potential to be detrimental to one's well-being (USEPA, 1989, 2001). The HI has been determined using the following Eq. (9) to measure the noncarcinogenic risk posed by various toxic metals.

$$HI = \sum_{i=1}^{n} HQ_i \tag{9}$$

where i represents different heavy metals.

The total HI for noncarcinogen from different exposure routes was computed using the following Eq. (10)

$$HI_t = \sum_{j=1}^n HQ_j \tag{10}$$

where *j* represents the different exposure pathways.

HI>1 shows that there must be a potential to cause adverse impacts upon exposure, whereas HQ < 1 means no adverse impacts can occur. The RfD_o , RfD_i , and RfD_{dermal} values for the heavy metals were presented in tables containing screening levels for heavy metals formulated by (USEPA, 2014) and are stated in Table S3. Moreover, probabilistic risk assessment was also carried out in order to estimate the likelihood of risk among workers due to heavy metals dust exposure. It is further explained in supplementary data section S8.

Statistical analysis

IBM-SPSS statistics version 20 was used for statistical analysis. Graphs were constructed using Microsoft excel 365 and origin Pro 2018. One-way ANOVA and independent t test were performed in order to determine significant differences among heavy metals from different sites. Monte Carlo simulations for probabilistic risk assessment and sensitivity analysis were run using Oracle crystal ball software version (11.1.2.4). Using the Origin Pro2018 software, the descriptions of probabilistic health risks are described in figures.

Results and discussion

Dust heavy metals content (<75 μm, 75–106 μm, 107–150 μm size fraction)

The mean concentrations of heavy metals in three size fractions of dust are depicted in Fig. 2a, b. In chromite mines, the highest concentration of Cr and lowest concentration of Cd were measured. Overall, the mean concentration decreased in the following pattern Cr>Mn>Zn>Ni>Pb>Co>Cu>Cd. Similar findings were previously reported in chromite mine in Pakistan where a high level of Cr (320 mg/kg) and the lowest level of Cd (2.55 mg/kg) were measured, and quite a similar trend Cr>Ni>Pb>Zn>Cd was observed (Nawab et al., 2016). Comparable to that, highest concentration of Cr (244 mg/kg) and lowest concentration of Cd (52 mg/kg) were also reported in India (Naz et al., 2018), whereas in coal mines, the highest concentration of Mn and lowest concentration of Cd was measured. Overall, concentration of heavy metals in coal mine decreased in the following manner Mn > Pb > Cu > Zn > Ni > Cr > Co > Cd. The trend was quite similar in all three size fractions of dust. Quite similar trend, i.e., Pb>Cu>Zn>Cr>Ni>Co>Cd, was also previously observed in coal mines of Cherat in Pakistan (Ishtiaq et al., 2018). Comparable to that, high concentration of Mn (658 mg/kg) was measured in coal mine-affected areas in India (Rout et al., 2013). This may attribute to the fact that manganese is present in carbonates. Due to various ongoing mining activities, the rocks may subject to weathering and might result in the enrichment of dust with toxic elements (Moreno et al., 2019; Trechera et al., 2020). Overall, a statistically significant difference (P < 0.05) is observed among heavy metals in three size fraction of dust between coal mines and chromite mines. However, no significant difference is observed among heavy metals in coal mines of different regions, i.e., Quetta, Khushab, Mianwali, and Chakwal. Statistical data for coal and chromite mines have been presented in supplementary data Table S4a, b.

A difference in mean concentrations between different size fractions (i.e., $<75 \ \mu\text{m}$, 75–106 μm , 107–150 μm) was observed. Moreover, statistical analysis also showed significant difference (P < 0.05) among three size fractions for both the coal and chromite mines. The smallest size fraction of dust ($<75 \ \mu\text{m}$) had an increased level of heavy metals as compared to size fractions 75-106 µm and 107-150 µm in both coal and chromite mines. According to the mean concentrations of heavy metals in three size fractions of dust, it is significant that heavy metal concentrations increased with decreasing size fractions. Several studies have shown that the finest dust fraction (63-75 µm) contains high levels of heavy metals (Lee et al., 2013; Niu et al., 2010; Singh, 2011). For instance, it has been reported that the amount of heavy metal content, i.e., Cu, Zn, Pb, and Cd, were found to be highest in small particles $(<150 \ \mu\text{m})$ (Li et al., 2015). Moreover, in another study, Cu, Sb, Sn, Pb, Zn, As, and Ni were found to be more concentrated in PM2.5 than in PM10 particle size that is more inhalable and can penetrate more easily (Moreno et al., 2019). As fine dust fraction is profoundly inhalable, thus it has more potential to act as a high bio-reactive fraction (Moreno et al., 2019). The results of this study also comply with the fact that high concentration of heavy metals tends to concentrate in the smallest size fractions Moreover, it has been reported that particles usually less than 100 µm can readily be resuspended and cling to the skin, while particles lesser than 63 µm can effectively bind and carry trace elements (Botsou et al., 2020). As a result, the emphasis of this study was on risk assessment and pollution assessment for the smallest size fraction $< 75 \,\mu m$.

Heavy metals composition ($<75 \mu m$ dust size fraction)

The range and the mean values of the analysed heavy metals in dust fraction <75 µm are presented in Fig. 2c, d. In chromite mines, the highest concentration of Cr (340.6 mg/kg) with the range 239.9-457.9 mg/kg and the lowest concentration of Cd (8.4 mg/kg) with a range of 3.4-13.5 mg/kg were measured. The concentrations of Co, Cu, Mn, Ni, Pb, and Zn were in the range 9.5–14.1, 6.3–11.4, 41.9-157.9, 15.4-42.7, 6.5-41.3, and 31.8-67 mg/ kg, respectively. From highest to lowest, the average concentration hierarchy of heavy metals was Cr (340.6 mg/kg)>Mn (93.8 mg/kg)>Zn (46.9 mg/ kg)>Ni (27.5 mg/kg)>Pb (21.7 mg/kg)>Co (11.4 mg/kg) > Cu (9.2 mg/kg) > Cd (8.4 mg/kg).There are no specific guidelines for heavy metals in the dust at the moment. However, the World Health Organization (WHO) has developed environmental



Fig. 2 Concentrations of heavy metals in examined mines: **a** mean concentrations of the heavy metals in three size fractions of dust in coal mines, **b** chromite mines, **c** box plots illustrating heavy metals concentrations in dust fraction with size <75 μ m in coal mines, and **d** chromite mines (the box determined 25th

and 75th percentiles, the whiskers determined 5th and 95th percentiles). The mean is indicated by the horizontal line inside the box, whereas the horizontal dotted line indicates the reference standard value. The asterisk represents the minimum and maximum values

quality criteria for soil that are used as basic reference values when measuring heavy metal pollution in the dust (Gao et al., 2020). The mean concentration of Cd and Cr was 2.8 and 3.4 times higher than their standard reference values, respectively. Chromium is primarily found in mafic and ultramafic rocks, where concentrations can reach 3000 mg/kg, which may lead to its high concentration in the dust (Alloway, 2013). In coal mines, the highest mean concentration of Mn (284.9 mg/kg) with a range of 252.2–309.8 mg/kg and the lowest mean concentration of Cd (2.1 mg/kg) with a range of 1.2-3.2 mg/kg were measured. Co, Cr, Cu, Ni, Pb, and Zn concentrations range from 10.4–16, 25.3-36.4, 41.9-55.5, 73.2-94.9, 110.6-147, and 52.8-65.5 mg/kg, respectively. Overall, mean concentration of heavy metals decreased in the following manner Mn (284.9)>Pb (125.5)>Ni (84.3)>Zn (58.1) > Cu (48.8) > Cr (30.2) > Co (13.6) > Cd (2.1).The mean concentrations of all heavy metals lie much below the standard reference values except for Ni and Pb which were 1.6 and 1.2 times greater, respectively. A high concentration of Pb and Ni in dust may be associated with vehicular movements in mining areas (Rout et al., 2013).

Pollution level assessment

Enrichment factor values of heavy metals are presented in Fig. 3a, b. In coal mines, EF values exhibited a range of 10.8-24.3 Cd, 0.14-2.3 Co, 0.6-1 Cr, 2.3-3.1 Cu, 0.6-0.9 Mn, 2.2-3.6 Ni, 12.3-18.9 Pb and 1.3-1.9 Zn. Generally, the EF values revealed a descending order as Cd>Pb>Ni>Cu>Co>Zn>C r. Significant enrichment was observed for Cd and Pb based on the degree of metal pollution and moderate enrichment was observed for Ni and Cu. This means that the increased levels of lead (Pb) in coal mines are mainly attributed to anthropogenic influences that might be due to vehicular movements. However, minor enrichment was observed for other metals Co. Zn, and Cr. High EF values indicate a greater anthropogenic influence (Sabouhi et al., 2020). In chromite mines, the enrichment factor exhibited the range of 8.3-41.8 Cd, 1.9-4.5 Cr, 0.1-0.2 Cu, 0.04-0.15 Mn, 0.15-0.49 Ni, 0.26-1.6 Pb, and 0.3-0.6 Zn. Generally, the EF values revealed a descending order as Cd>Cr>Pb>Ni>Zn>Co>Cu>Mn>Cd. Severe enrichment and moderate enrichment were observed for Cd and Cr, respectively. Moderate chromium enrichment demonstrates that the contribution of anthropogenic effect is considerably insignificant. The reason for this is that Mafic and ultramafic rocks are present in chromite mining sites, and high concentrations of chromium in such rocks can range up to 3000 mg/kg, which might be released during mining processes (Alloway, 2013). Previously a study in India also reported significant and moderate enrichment for Cr and Ni, respectively (Pattnaik & Equeenuddin, 2016).

The geo-accumulation index's average values are shown in Fig. 3c. Table S1 shows different classes for pollution levels. In chromite mines, the highest value was found for Cr (1.2) and lowest for Cd (-2.2). The Igeo values presented a descending order Cr> Pb>Zn>Ni>Mn>Co>Cu>Cd. The dust was categorized as moderately polluted regarding Cr while the rest of the heavy metals falls in the category of unpolluted to moderately polluted except for Cd, whereas in coal mines, the highest value was found for Pb (1.5) and lowest for Cd (-0.8). Igeo values revealed descending order Pb>Cu>Ni>Zn>Co> Cr > Mn > Cd. The data revealed that the majority of the dust samples were classified as "moderately contaminated" regarding Ni and Pb. Even though the petrol utilized in vehicles is free of Pb, the less solubility of already existing Pb makes it stay in soil and dust for a longer time (Masto et al., 2017). Moreover, dust produced due to the activities carried out through automobiles could be the source for Ni (Rout et al., 2013). On the contrary, all dust samples revealed negative values of the geo-accumulation index for Cd and hence classified as non-polluted. This study's results are in line with previous studies that reported dust in the coal mine was unpolluted to moderately polluted with Cu, Co, Cr, and Zn (Tang et al., 2017). Accumulation of Pb and Ni in coal mines needs further attention as their concentration in dust also exceeds its reference standard values posturing a threat to human health.

Exposure assessment

The calculated hazard quotient (HQ) of heavy metals for mine workers is illustrated in Fig. 4a, b and presented in Table S5. It shows the contribution of different pathways in the overall risk. In chromite mines, the highest HQ value was observed for Cr while in coal mines it was found for Pb. High exposure due Fig. 3 Pollution levels assessment of examined mines **a** box plots illustrating enrichment factor in coal mines (size fraction <75 μ m), **b** chromite mines (size fraction <75 μ m), and **c** scatter plots of Igeo values for eight heavy metals in examined mines in size fraction <75 μ m



to contaminated dust was attributed to higher heavy metal concentrations in the dust as a result of ongoing mining activities (Ishtiaq et al., 2018). Ingestion, rather than inhalation or dermal absorption, appeared to be the most common exposure route for both coal and chromite mine workers. Moreover, Mn inhalation appeared to contribute to some extent to the overall health risk in coal mines while dermal absorption was found to significantly contributing in the case of Cd and Pb. Overall, in comparison with ingestion and dermal pathways, the HQ due to inhalation was much lower. According to similar findings, the risk of heavy metal exposure through inhalation is almost negligible when compared to the other two paths (Rout et al., 2013; Zheng et al., 2010). Moreover, increased intake was found through the ingestion route which is consistent with previous findings from Pakistani mining areas (Ishtiaq et al., 2018) and northern Spain (Ordóñez et al., 2011). Overall, estimated HQs of the heavy metals in chromite mines were significantly higher than that of coal mines implying that workers in chromite mines were at higher risk of getting adverse effects. A possible explanation of this might be that the heavy metals level in chromite mine is higher so the workers were subjected to higher doses of heavy metals. For Cr in chromite mines, the HQ even surpassed the safe level (HQ=1) signifying that it can potentially cause adverse health effects in mine workers. Moreover, the HI for rest of the heavy metals exhibited values less than 1 signifying no negative



Fig. 4 Multi-element analysis of the hazard quotient and HI in examined mines. a Average hazard quotients (HQs) estimated for the exposed workers in coal mines, b chromite mines, c average HI estimated for the workers in coal mines, and d chromite mines

consequences. Overall, exposure through different pathways was in the order of ingestion > dermal absorption > inhalation. This result is similar to that of previous studies that have looked at toxic metals in street dust in an industrial area (Lu et al., 2014) and different functional zones in Beijing, China (Wei et al., 2015). Human exposure through dust during work time led to the risk in the order as Pb>Cr>N i>Cd>Mn>Cu>Co>Zn and Cr>Cd>Pb>Ni >Mn>Co>Cu>Zn for coal and chromite mines, respectively.

Health risk assessment

The health risks of heavy metals were estimated by deterministic method for three pathways, i.e., ingestion, inhalation, and dermal absorption using equation. The acceptable or tolerable risk given by USEPA is 1, which shows that humans are unlikely to get significant adverse health effects if the risk value is less than 1. However, if the risk value is above 1 it significantly causes health impacts in humans (Imran et al., 2020). Figure 4c, d presents the risk of exposure to various dust-bound dust fractions in coal and chromite mines with respect to different heavy metals. The estimated mean HI results are given in Table S6. Different size fractions of dust had a different impact on coal and chromite mine workers. For instance, for chromite mines, the estimated total HI was 1.4, 1.2, and 1.1 for <75 µm, 75–106 µm, and 107–150 µm size fractions, respectively. For dust fraction $< 75 \mu m$, the risk associated with human health showed a decreasing trend Cr (1.2)>Cd (1.5E-1)>Pb (6.6E - 2) > Ni(1.6E - 2) > Mn(7.7E - 3) > Co(6E-3)>Cu (2.4E-3)>Zn (1.6E-3). The HI ranged from 0.001 to 1.92. In the risk assessment of dust heavy metals, particle size plays an important role (Cao et al., 2012). Smaller particles tend to deposit at low rates as compared to big particles thus having a longer residence period in air, thereby affecting human health adversely (Gustafsson et al., 2018). In coal mines, the estimated total HI was 6E - 1, 3.1E-1, and 1.9E-1 for <75 µm, 75–106 µm, and 107-150 µm size fractions, respectively. This shows that as the size of dust decreases the HI increases signifying that smaller particle has more potential to cause adverse impacts in humans (Doyi et al., 2020). For dust fraction $< 75 \,\mu$ m, the risk decreased in order as Pb (3.8E-1)>Cr (1E-1)>Ni (4.8E-2)>Cd (3.5E-2) > Mn (2.3E-2) > Cu (1.3E-2) > Co(7.2E-3) > Zn (2E-3). The HI ranged from 0.002 to 0.73 with a mean value of 0.3.

The concentration of heavy metals in a fraction increases as the particle becomes finer. (Li et al., 2015). Elevated HI values of Cr (HI > 1) in chromite mine contrasted to the rest of the heavy metals might be due to their greater intake and their low reference dose values (Khan et al., 2013). The overall health risk to HMs for chromite mine workers is nearly twice as high as the projected risk for coal mine workers, and it also exceeds the safe levels (HI=1), indicating negative health effects. Previously reported, in street dust from a coal-mining city in eastern China, the total HI from ingestion, dermal contact, and inhalation measured from 0.142 to 0.322, suggesting no health risks to adults in the region (Tang et al., 2017). Likewise, elevated HI levels of Pb, Cr, and Cd were reported in coal mining areas of Cherat in Pakistan (Ishtiaq et al., 2018). The health risk for coal and chromite mine workers was also evaluated using Monte Carlo simulations which take into consideration the variability and uncertainty related to input parameters, i.e., exposure time, body weight, ingestion rate. Cumulative probabilities for risk are shown in Fig. 5a, b. In coal mines, the accumulative risks at P50 due to the eight metals were probable to be 2.91E - 03 - 2.42E - 03. The average HI values for ingestion, inhalation, and dermal absorption routes of heavy metals were 7.40E-01, 2.26E-03, and 4.41E-02, respectively. Exceeding values of HI for ingestion revealed that it is a predominant pathway that plays a major part in causing risk during occupational exposure. In chromite mines, the accumulative risks at P50 due to the eight metals were probable to be 8.79E - 01 - 1.74E + 00. The average HI values for ingestion, inhalation, and dermal absorption pathways of heavy metals are 1.35E + 00, 1.98E - 03, 6.33E - 02. There are more than 80% chances that HI exceeds the safe level (HI > 1) through the ingestion pathway.

Sensitivity analysis

This analysis aimed to determine the impact of input parameters on health risk assessment. The sensitivity of each exposure parameter was determined using the spearmen's rank correlation coefficient process. Negative and positive tornado plots were used to present



Fig. 5 a Cumulative probabilities of noncarcinogenic risks to the workers in coal mines (size fraction $<75 \mu$ m), **b** chromite mines (size fraction $<75 \mu$ m), **c** sensitivity analysis

the findings. These are presented in Fig. 5c, d. The importance of presenting the data such layout is that the related risks are more obvious and it gives like-liness for risk when input parameters fluctuate (Pask et al., 2017). The most significant parameter contributing to health risk in both coal and chromite mines is the concentration that is 20.5% and 20.4%, respectively. Moreover, in the case of coal mines ingestion rate, exposure duration, and exposure frequency also contributed to health risk with a mean sensitivity

for dust health damages to workers in coal mines (size fraction ${<}75~\mu m),$ and d chromite mines (size fraction ${<}75~\mu m)$

of 18.9%, 18.3%, and 3.4%. On the contrary, body weight and average time exhibited negative sensitivity with a mean of -19.7% and -19%. In chromite mine, most influential parameters followed by concentration are ingestion rate (19.9%), average time (-19%), exposure duration (18.7%) body weight (-18.4%), and exposure frequency (3.6%). The most influential parameters are average time and concentration contributing to the health risk of both coal and chromite mine workers. They show significant effects, and such

findings may help relative authorities and managers to devise effective measures to limit the health risk to exposed heavy metals (Tong et al., 2019).

Limitations

However, further work needs to be done to ensure that dust health risk evaluations provide more accurate and comprehensive results. For example, this study primarily focused on the dust fraction <75um, which is still a larger particle size, as there are finer particle fractions, such as PM₁₀ and PM_{2.5}, that may have more adverse effects on human health. Certain implications exist when studying fractions of smaller scale, such as PM2.5 or PM10, which necessitate comprehensive sampling involving instruments with continuous power supplies. Second, these areas are typically challenging to reach due to low subject participation, making small sample sizes difficult to obtain. It is, however, the first research to document heavy metals related risks in mining areas. Future studies should focus to compare heavy metal levels in smaller size dust fractions to get a better understanding of contamination in occupational settings.

Conclusion and recommendations

This study utilized the USEPA risk valuation model and the Monte Carlo simulation model to find out noncarcinogenic risks associated with heavy metals among workers in coal and chromite mines using various dust fractions, i.e., <75 um, 75-106um, and 107-150um. Results revealed that elevated levels of heavy metals were concentrated in finer dust particles. Both deterministic and probabilistic methods showed that ingestion was observed to be the most dominant pathway contributing to health risk assessment. The health risk assessment for Cr in the chromite mine revealed significant noncarcinogenic risks. Keeping in view the results of sensitivity analysis that shows concentration and exposure time to be the most influential parameters contributing to risk. The study implies that generation of heavy metals contaminated dust is a serious problem in mining areas and should be monitored continuously. Furthermore, the health risk caused by exposure to the smallest size dust fraction should be thoroughly investigated. To lessen the health risks associated with occupational exposure, contemporary and efficient technologies must be employed and the use of personal protective equipment should be made obligatory among workers to limit heavy metals exposure. SOPs should be formulated and followed to restrict the prolonged exposure to high concentrations of heavy metals to the workers.

Author contributions ZS: Contributed to writing original draft, data curation, analysis. MYAR: Contributed to study design, writing, review, and editing. HKK: Contributed to review and editing. RNM: Contributed to conceptualization, supervision, study design, and review.

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Data availability All the supporting information is including in supplementary information. Any additional information or data can be provided upon request.

Declarations

Conflict of interest The authors have not disclosed any competing interests.

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