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CONTAMINATION AND HEALTH RISK ASSESSMENT OF HEAVY METALS FORM A TYPICAL Pb-Zn SMELTER IN NORTHWEST CHINA

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Abstract

Soil contamination by heavy metals due to metal smelting activities poses a serious threat to the ecological environment and to human health, as it is considered to be one of the most significant sources of soil pollution. The objective of this study was to analyze the pollution status and human health risks of heavy metals emitted from metal smelting activities of a Pb-Zn smelter. The results of mean values of Zn, Pb, Cd, Cr, Cu and Mn should be incorporated and mention the status in respect to background value. Contamination levels of heavy metals were evaluated using the potential ecological risk index (RI). Possible human health risks were assessed using the health risk assessment model developed by the US EPA. The results showed that the soils are seriously polluted, and migrated down the soil vertical profile. The index of RI indicated a very high potential ecological risk overall in the entire study area, especially for Cd. The health risk analysis showed that adults and children are exposed to significant non-carcinogenic health risks, and there are higher non-carcinogenic health risks for children than for adults. Additionally, the carcinogenic risks of Cr were higher than those of Cd for the two population groups, and children were more susceptible than adults. These results are useful for management, prevention, control and remediation of heavy-metal contamination. Meanwhile, this research provides methods, experiences, and reference to other study of similar heavy-metal soil pollution.

Introduction

With the rapid development of industrialization and urbanization in developing countries, large amounts of heavy metals (HMs) produced by anthropological activities enter into the environmental medium, which becomes polluted or causes adverse ecological effects when it exceeds the load of the environmental medium (Gao *et al.* 2014, Salmanighabeshi *et al.* 2015, Agomuo *et al.* 2017, Li *et al.* 2018). Currently, soil contamination by HMs has more invisibility and great harmfulness and is regarded as the most adverse environmental issue in the universe, not only because of its acute and chronic toxicity to plants, animals, microorganisms, and the ecosystem but also because of its environmental persistence, bioaccumulation, non-degradable and slow removal process (Islam *et al.* 2015, Islam Md *et al.* 2018, Nkansah *et al.* 2017, Moghtaderi *et al.* 2018, Ataullah *et al.* 2018). Numerous previous studies have shown that HM pollution in soil has been both serious and widespread in many areas in China, which has become a severe obstacle for regional economic and social development and human health (Li *et al.* 2014, Li *et al.* 2016, Padoan *et al.* 2017, Wu *et al.* 2018, Steffan *et al.* 2018, Xu *et al.* 2018, Yang *et al.* 2018). According to the State Environmental Protection Administration, China faces serious soil HM pollution; approximately 10 million m^2 of arable land has been polluted, and 12 million tons of grains have been contaminated by HMs in the soil in China (Teng *et al.* 2010, CSC 2012, Chen *et al.* 2015, Li *et al.* 2018). The HM pollution in China has drawn worldwide attention. Many investigations have confirmed that mining activities (including excavating, crushing, grinding, separation, smelting, refining and tailings) are the primary source of HMs in the environment, which pose the greatest

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potential risk to human health and the environment (Ramana *et al.* 2012 and 2013, Ettler *et al.* 2014, Li *et al.* 2015, El Azhari *et al.* 2017, Shen *et al.* 2017, Ahirwar *et al.* 2018, Gu *et al.* 2018, Lee *et al.* 2018, Zhu *et al.* 2018). In many pollution sources and paths, activities associated with mining, including industrial mining, metal flotation, smelting and processing, artisanal gold mining, and uranium mining, have been regarded as four of the world's ten pollution problems (Ericson *et al.* 2008, *Csavina et al.* 2012). All mining exploitation, including mining, crushing, grinding, screening, smelting, refining, casting, metal processing and tailings management, and even including the transportation of ore, produce large quantities of dust and aerosols with high levels of heavy metals, which are released into the air and deposited as dust. Atmospheric particles discharged into the air by mining activities are as an important component of air pollution, and even affect the entire biosphere, including atmosphere, hydrosphere, and pedosphere. Mineral dust is one of the primary contributors of atmospheric aerosol. Dust and aerosols from mining activities are normally associated with significantly elevated levels of one or more of these contaminants including Pb, Cr, Hg and As (Meza-Figueroa *et al.* 2009, Brotons *et al.* 2010, Corriveau *et al.* 2011). A great deal of dust loaded high levels of heavy metals can be released into the air and deposited on the surface of the soil as dust as a result of mining activities, including mining, crushing, grinding, screening, smelting, refining and tailings management, and enter into soil via deposition and precipitation (Csavina *et al.* 2012, Li *et al.* 2015). In particular, the smelting of metal ores is consider as one of the most serious sources in all HM pollution sources. The smelting of ore concentrates powder causes large quantities of Pb, Zn, Cd, Cu, As and Hg, and other elements to be released into the environment, which can cause bioaccumulation and bio-magnifications in the ecosystem (Shang et al. 2017). The high concentration of Pb, Cd, Cu, Cr and As have been considered as poisonous and harmful heavy metallic elements to human health by the World Health Organization (WHO) (Song et al. 2015). In addition, Pb, Cr, As, Hg, pesticides, and radionuclides are considered as the six most toxic pollutants that threaten human health (McCartor and Becker 2010). Many investigations have indicated that there is a relationship between mortality and living near mining and smelting areas (Hawkesworth *et al.* 2013, Song *et al.* 2013, Song *et al.* 2015). The dust and aerosol particles from mining activities may carry highly toxic metallic and nonmetallic elements, including the neurotoxic elements such as Pb and As, which are easy to accumulate in sediment and vegetation. There are three main size ranges in atmospheric dust and aerosol, including ultrafine, accumulative and coarse, and all of these types of patterns are closely related to mining-related emission (Křībek *et al.* 2010, Csavina *et al.* 2012). Among them, ultrafine particles are mainly generated from hot vapors in the smelting furnace, which diffuse quickly into the air, and they would collide and coagulate into larger particles at residence times in the air of minutes to hours, form accumulative particles. The accumulative particles are too large to diffuse or coagulate in a short time, but they are too small to settle by gravity, so they remain at an average residence time of 8-10 days in the air. However, coarse dust are mainly generated by crushing and grinding of ore and wind erosion of mine tailings, which settle rapidly into soil and water in minutes to hours. Researches have also confirmed that the particle sizes of dust and aerosols can affect the deposition efficiency (Krombach *et al.* 1997, Park and Wexler 2008, Valiulis *et al.* 2008, Csavina *et al.* 2012). Besides, epidemiological studies showed that ultrafine dust may has much effect on the health (Shaheen *et al.* 2005, Moreno et al. 2006, Querol *et al.* 2006, Csavina *et al.* 2006). Moreover, heavy metal elements in soil and atmospheric particulates easily enter into the human body by inhalation, ingestion and dermal contact, and might lead to poisoning or even death if people excessively intake of these elements, especially in children (Lu *et al.* 2009, Ali Ubaid *et al.* 2017, Doabi *et al.* 2018, Li *et al.* 2018a, Steffan *et al.* 2018). In recent years, the problem of HM pollution have become increasingly serious, and protecting environment from pollution and ensuring people to keep healthy have become a problem needed to address urgently (Duan *et al.* 2016, Akopyan *et al.* 2018, Li 2018). Although some studies have analyzed and assessed the pollution levels, spatial distribution state, potential risks, and health risks of heavy metals from mining and smelting area soil, the regions of heavy metals contamination from mining activities have received relatively less attention.

Baoji is rich in mineral resources of many varieties and is main a base of lead-zinc minerals in China. In the course of the exploitation of metal ore, the environment could been vulnerable to pollute in these areas and its surroundings. Emissions of heavy metals can pollute atmosphere, soils, surface water, groundwater, and food crops, even which can threaten the health to residents near mining areas. Feng County (33°34′50″-34°18′13″N, 106°24′19″-107°10′26″E) is located to the southwest of Baoji City in the Shaanxi Province of China. Feng County is much enriched in lead-zinc (Pb-Zn) mineral resources and deposits probably reached 4.5 million tons, as one of the four biggest Pb-Zn mineral bases in China (Shen *et al.* 2017, Fan *et al.* 2019). One of the largest Pb-Zn smelters in Baoji is located in Feng County. The Pb-Zn smelter lies in a canyon area, which is dominated by mountains. The refining dusts and exhaust gases are difficult to diffuse, and those refining dusts contain toxic and harmful heavy metals such as Pb, Zn, and Cd. Long-term mining activities have caused serious pollution of this area, and ever the accidents of excessive amounts lead in the blood occurred in 2012 (Shen *et al.* 2017, Fan *et al.* 2019). Shen *et al.* (2017) studied the physicochemical parameters of soil, spatial-temporal distributions of HMs and potential ecological risks in this smelter area three years ago. Even now, the Pb-Zn smelting activities are ongoing. Although the smelting process has been considerably improved and the metalliferous dust emission significantly decreased, the soil has still been contaminated in recent years. The soil contaminated by Pb-Zn smelting activities still needs to be further investigated, and this information is very important to control and manage the contaminated lands and to provide a theoretical basis for management, prevention, control and remediation of heavy-metal contamination in the future.

The present research has been under taken to: (1) quantify the concentrations of heavy metals such as Zn, Pd, Cd, Cr, Cu and Mn in the soil; (2) evaluate the enrichment degree of the heavy metals studied; (3) assess the ecological risk of HMs; and (4) evaluate the health risks from exposure to HMs in the Pb-Zn smelter located in the northwest part of Feng County in Northwest China.

Materials and Methods

The concerned Pb-Zn smelter located in the northwest part of Feng County at longitude 106°32′2.69″(E) and latitude 33°56′43.02″(N) is approximately 3 km north of the county (Fig. 1). The Pb-Zn smelter started to be built in 2000 and was started in 2001 by the Dongling Group subsidiary. The smelter mainly engaged in nonferrous metal smelting, sulfuric acid production, coking production, calcine and other zinc byproducts, with annual output of 6.0×104 tons zinc and 1.2×105 tons sulfuric acid in recent years. There was a village to the north at about 350 m; however, most of the inhabitants have long since been evacuated, leaving only a few people. The north soil near the smelter was once used for agriculture; however, this area was planted with poplar forests to currently suppress smelter dusts. The west is near the Hong Tang Shuang Road. The XiaoRui River flows through the west of the Pb-Zn smelter from north to south, which flows into the Jialing River. The Pb-Zn smelter is located at the bottom of a canyon, and mountains are to its east. The smelter is still currently in production. This area lies among the mountainous and mild climate, with an average annual temperature of about 11.4°C. The mean annual precipitation is approximately 613.2 mm. The annual dominant wind direction is east winds and southwest winds, with an annual mean wind speed of 0.7 m/s.

Sampling was conducted from April to May 2017. Altogether 138 soil samples were collected using a stainless-steel drill from the soil around the Pb-Zn smelter in Feng County, including 46 surface soil (0–20 cm) and 92 related vertical profile soil (0-60 cm, with one soil sample was extracted per 20 cm). In order to make the taking of samples homogenous and representative, we collected 3 samples from each sampling site, and mixed together as one sample to provide the individual composite samples for the study. All the samples were placed in cloth bags respectively, and properly labeled and recorded, then transporting to our laboratory.

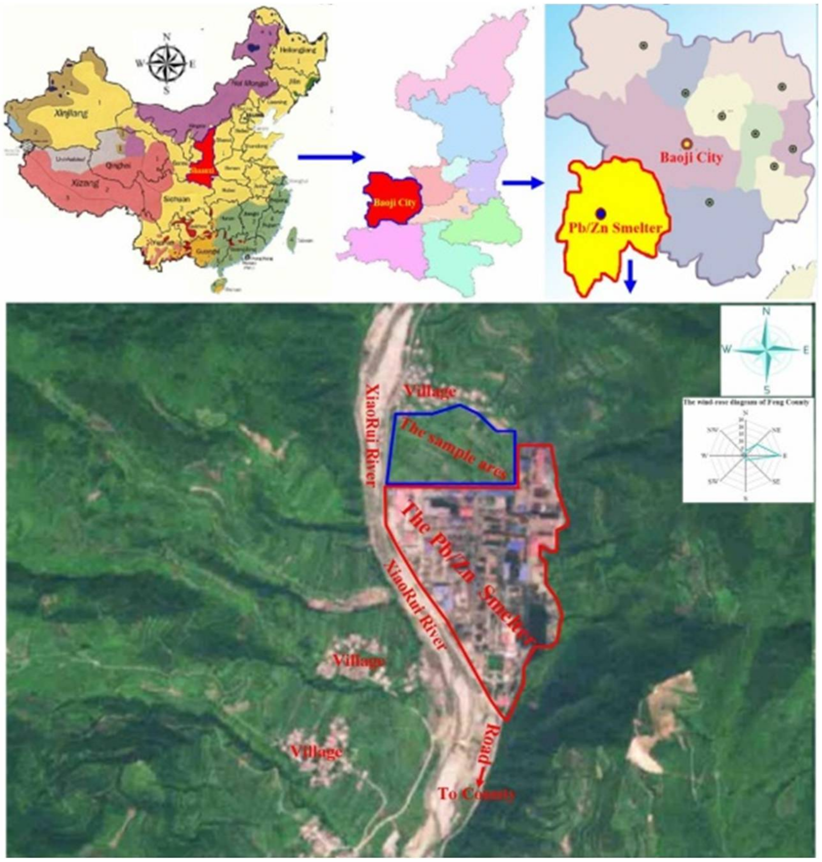

Fig. 1 The location of the studied regional

The collected soil samples were naturally dried to a constant weight in a dark place in the laboratory with indoor ventilation at room temperature. They were constantly crushed with hand in the natural drying process, and pick out stones, plant root residues and tree leaves. All the samples were crushed into power with a round wooden, and passed through a 0.15-mm (100-mesh) nylon sieve, storing in labeled cloth bags for analysis.

After a pretreatment, all soil samples were digested with HCl-HNO_3-HF-$HClO_4$ (volume ratio of 2:1:1:1) wet digestion. The detailed extraction procedure was described by Fan *et al.* (2019). Finally, all extracting samples were filtered using a 0.45-μm pore size cellulose acetate filter, and the filtrate was collected into acid-washed polyethylene sample bottles for HM analysis. The content of Pb, Zn, Cd, Cr, Cu and Mn was determined using an air-acetylene flame atomic absorption spectrophotometer (SHIMADZU AA-6800).

In this study, all reagents were guaranteed reagent (GR) grade, and all the chemical solution was prepared with ultra-pure water. All the glassware were soaked with 1% nitric acid for 24 h, then washed with ultra-pure water and dried in a drying oven. The errors from reagents and methods were reduced with analysis of replicates and the method blanks. Quality assurance and quality control were controlled using certified reference materials for the soils (GBW08301, supplied by the National Research Center for CRMs in China) that were used to verify the accuracy of the method. The recoveries were accepted when the determined standard concentrations for Pb, Cd, Zn, Cu, Cr and Mn were within 95~105% of the certified limits. The recoveries of Pb, Cd, Zn, Cu, Cr and Mn in our study ranged from 98.6 to 103.7%, 97.5 to 103.2%, 96.2 to 105.9%, 99.3 to 104.9%, 98.2 to 104% and 95.3 to 104.2%, respectively. Therefore, the errors from instruments were negligible in our study. Moreover, the preparation and analysis of each sample was analyzed in triplicate.

To ensure the sensitivity and stability of analytical instruments, a standard reference solution was analyzed after every 10 samples. The $mg \cdot kg^{-1}$ in this study means the contents of HMs in per kilogram of dry soil

Soil contamination degree is usually assessed by comparing the measured values of pollution status for HMs with the geochemical background values. Currently, there are various indices for evaluating the pollution extent of HMs. In order to understand the level of pollution of HMs and the toxic effect of HM pollutants for the environment, the potential ecological risk (PER) index were used in this study.

On the basis of sedimentology, Håkanson (1980) established the potential ecological risk index (RI), which was introduced to evaluate the contamination level of analyzed HMs in sediments. RI is the total potential ecological risks of all HMs, representing the sensitivity of biology community to toxic substances and illustrating the potential ecological risk caused by the contaminants (Yi *et al.* 2011, Bahloul *et al.* 2018, Barkett *et al.* 2018, Izah *et al.* 2018, Li *et al.* 2018(b)). Håkanson (1980) established three Eqs. (3-5) to calculate RI. E_r^i (Eq. 4) is calculated based on the contamination factor (C_f^i) of the element (Eq. 5).

$$RI = \sum_{i=1}^{n} E_r^i \qquad (3)$$

$$E_r^i = T_r^i \times C_f^i \qquad (4)$$

$$C_f^i = C_s^i \big/ C_n^i \qquad (5)$$

where n is the number of studied HMs; i is the ith studied element; RI is the potential ecological risk index of the HM; E_r^i is the potential risk factor for the individual HM; T_r^i is the toxic-response factor of an HM, which was given by Håkanson (1980) (i.e., Pb, Cu, and Ni=5, Zn=1, Cd=30, Cr=2, and As=10), accounting for the toxic requirement and the sensitivity requirement, reflecting the toxicity level and environmental sensitivity of the HM; C_f^i is the contamination factor; C_s^i is the actual concentration of the HM in the soil, mg·kg-1; C_n^i is the mean background concentration of studied element, mg·kg-1. The soil background values of elements used were those reported by Xue (1985) and the limiting value of II level standard of

State Environment Standard (GB156182-1995) (Table 2). According to Håkanson (1980), the E_r^i and RI can be classified into five categories, and classified as: low risk($E_r^i < 40$, RI$<$150); moderate risk(40$\leq E_r^i < 80$, 150$\leqslant$RI$<$300); considerable risk(80$\leq E_r^i < 160$, 300$\leq$RI$<$600); high risk(160$\leq E_r^i < 320$, 600$\leq$RI$<$1200); very high risk($\geqslant$320, RI$\geq$1200).

Human health risk assessment is to estimate the probability of adverse health effects in humans who may be exposed to harmful and toxic substances in contaminated environment (Li *et al.* 2014, Fan and Wang 2017, Li *et al.* 2018, Fan *et al.* 2019). Human health risk from direct exposure to the HM contaminated soil should not be ignored. In general, humans are three main pathways to expose in soil contaminated with HMs, including ingestion, inhalation and dermal contact (Fan and Wang 2017, Jang *et al.* 2017, Li *et al.* 2018). Ingestion through the mouth is the highest of all exposure pathways caused by soil pollution. In order to systematically understand the adverse effects caused by soil contamination with HMs and to protect human health, we have the necessity to carry out human risk evaluations of soil contaminated with HMs. The steps of a health risk assessment are as follows: risk identification, dose-response estimation, exposure assessment, non-carcinogenic risk assessment and carcinogenic risk assessment. Seven HMs of Cd, Cr, As, Pb, Cu, Zn, and Ni were preferentially considered in the health risk assessment, mainly because these heavy metals are relatively strong toxicity to humans, and there are detailed and published dose-response relationships (Ordóñez *et al.* 2011, Jang *et al.* 2017). The model used for human health risk assessment was originally formulated and recommended by the United States Environmental Protection Agency, and published the assessment guidelines and Exposure Factors Handbook of the US Environmental Protection Agency (USEPA 1986, 1989, 2001, 2002, 2003, 2004, 2011, Hadzi *et al.* 2018). In this study, the health risk assessment model recommended by the USEPA was used to evaluate the health risk from soil contaminated with HMs. In consideration of behavioral and physiological differences, the health risk assessment was divided into two groups of children and adults in this study.

In this study, the risk assessment to human health from the exposure of pollution was characterized using exposure assessment, non-carcinogenic risk and carcinogenic risk.

Human health exposure risk has close relation with exposure frequency, exposure time, exposure does, and exposure path. The purpose of exposure assessment is qualitative and quantitative to determine exposure risk from soil contaminated with HMs.

Dose-response assessment is to quantitatively evaluate the relationship between the exposure level of harmful factors and the incidence of health hazard effects on exposed humans, with the foundation for the quantification of the health risk assessment (Li et al. 2018). Different dose response may be due to the toxicity degrees of different elements and total intake of toxicity elements. Moreover, the behavioral and physiological effects of different people are different for different dose responses. Thus, this study divided the affected populations into children and adults, and respectively evaluates their health risk.

The risk exposure pathways caused by HM contaminated soils may occur in three main pathways: (a) direct ingestion of soil particles, termed ingestion; (b) inhalation of suspended particles through the mouth and nose, termed inhalation; and (c) dermal absorption of toxic elements from particles adhered to exposed skin (Ordóñez *et al.* 2011, Li *et al.* 2014). The research results of Ordóñez *et al.* (2011) showed that direct ingestion of soil particles is the most common risk exposure pathway for Pb, Cd, Zn, Cu, Cr, Ni and As for the mercury mining areas of Northern Spain. According to the human health risk evaluation manual (Part A) and supplemental guidance for dermal risk assessment (Part E) (USEPA 1989 and 2004), the average daily dose

(ADD) of HMs via each pathway can be calculated as follows (Li *et al.* 2015, Han *et al.* 2017, Moghtaderi *et al.* 2018):

$$ADD_{ing} = C \times \frac{IR \times EF \times ED}{BW \times AT} \qquad (6)$$

$$ADD_{inh} = C \times \frac{IR \times EF \times ED}{BW \times AT \times PEF} \qquad (7)$$

$$ADD_{dermal} = C \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \qquad (8)$$

$$ADD = ADD_{ing} + ADD_{inh} + ADD_{dermal} \qquad (9)$$

where ADDing, ADDinh, and ADDdermal are the average daily intake doses of HMs from soil via ingestion, inhalation, and derma, respectively, with units of mg/kg/d; C is the measured concentration of HM in the soil, with units of mg/kg; ADD is the sum of the average daily intake soil doses via the three pathways; IR is the ingestion rate from soil contaminated by HMs, with units of mg·day-1; EF is the exposure frequency, with units of days·year-1; ED is exposure duration, with units of years; BW is the body weight of the exposed individual, with units of kg; AT is the average contact time, with units of day; SA is the individual exposed skin surface area, with units of cm2·day-1; AF is the skin adherence factor, with units of mg/cm^1/day; PEF is the particle emission factor, with units of m^3/kg; and ABS is the dermal absorption factor, unitless. Table 1 shows the various parameter values for the two calculation formulas.

Table 1. Exposure dose of health risk assessment models.

Factor	Values (children)	Values(adults)	Reference
EF	350 days/year	350 days/year	Environmental site assessment guideline (2009)
IR	200 mg/day	100 mg/day	USEPA 2011
PEF	1.36×10^9	1.36×10^9	USEPA 2011
ED	24 years	6 years	USEPA 2011
SA	2800 cm^2/day	5700 cm^2/day	Environmental site assessment guideline (2009)
AF	0.2 mg/cm^{-2}	0.07 mg/cm^{-2}	USEPA 2004
BW	15 kg	70 kg	Environmental site assessment guideline (2009)
AT	ED×365 (Noncarcinogenic); 70×365 (Carcinogenic)		USEPA, 1989
ABS	0.001	0.001	Chabukdhara and Nema 2013

According to the health risk evaluation model recommended by the USEPA, the human health risk from the HMs was classified into non-carcinogenic risk and carcinogenic risk. In this study, hazard quotient (HQ) was used for evaluation the non-carcinogenic risks caused by the contaminated soil with HMs. The values of hazard index (HI) equal to the sum of all HQs from the three main exposure pathways, with meaning the total potential non-carcinogenic risks of all the elements studied. HQ and HI were used to estimate the non-carcinogenic risk. The non-carcinogenic risks of the HMs are given as Formulas (10)-(11).

$$HQ_{ij} = \frac{ADD_{ij}}{RfD_j} \qquad (10)$$

$$HI = \sum_{i=1}^{n}\sum_{j=1}^{3} HQ_{ij} = \sum_{i=1}^{n}\sum_{j=1}^{3} \frac{ADD_{ij}}{RfD_j} \qquad (11)$$

where ADDij is daily intake of a certain toxic metal (i) through an exposure pathway (j); HQij is the noncarcinogenic risk that estimates the risk level for the single element (i) in an exposure pathway (j), which equal to divide the average daily dose by a specific reference dose (RfDj); RfDj indicates the exposed populations intake the toxic elements maximum levels that didn't cause adverse reactions via an exposure pathway (j) in unit weight and unit time, with units of mg·kg-1·day-1, the values of RfDj in this study are as follows: RfDing, Pb=3.50×10-3, Zn=3.00×10-1, Cd=1.00×10-3, Cr=3.00×10-3, Cu=4.00×10-2; RfDinh, Pb=3.52×10-3, Zn=3.00×10-1, Cd=1.00×10-3, Cr=2.86×10-5, Cu=4.02×10-2; RfDdermal, Pb=5.25×10-4, Zn=6.00×10-2, Cd=1.00×10-5, Cr=6.0×10-5, Cu=1.20×10-2(USEPA 1989, 1996, 2004; Bai et al. 2017; Li et al. 2018(b); Moghtaderi et al. 2018). HI represents the total noncarcinogenic risk from the three exposure pathways of all individual toxic metal; and i represent the different contaminants. Generally, HQ or HI < 1 means that there is no possibility of adverse health effects for exposed populations, whereas a HQ or HI > 1 may be possible adverse health effects (USEPA 1989).

The cancer risks were used to signify the carcinogenic effects. The carcinogen risk (RI) reflects the caused cancer probability of the populations exposed to the potential carcinogen within the entire lifetime. In assessment models of RI, the values of RI represent a level of cancer risk, which are equal to the exposure doses of each exposure pathway are multiplied by the slope coefficient (SF). The SF shows the maximal probability of the carcinogenic effect for the human body upon exposure to a certain dose of pollutant, with units of mg/kg/day (USEPA 2002). According to the USEPA, Cd, Cr, Co and Ni are considered carcinogens only via inhalation, therefore, we only consider the carcinogenic risk of Cr and Cd in this study, and the SF values of the studied metals are SFinh-Cd=6.30 and SFinh-Cr=42.00. The carcinogenic risk levels are divided into five categories. RI values below 10-6 show there are no significant health effects, and this is also set as the maximum limit of the acceptable risk level for carcinogens by the USEPA. Then, 1×10-6–1×10-5 indicates low risk, 1×10-5–1×10-4 indicates medium risk, 1×10-4–1×10-3 indicates high risk, and >10-3 indicates very high risk and is perceived as being concerning and needs an effective method for reducing the exposure and resulting risk (Rapant *et al.* 2011, Li and Ji 2017, Han *et al.* 2017, Tepanosyan *et al.* 2017). The following formulas (12~13) are used to calculated the carcinogenic risk of Cr and Cd (USEPA 1989).

$$RI_{ij} = ADD_{ij} \times SF_{ij} \qquad (12)$$

$$RI = \sum_{i=1}^{n} ADD_{ij} \times SF_{ij} \qquad (13)$$

where RIij is the carcinogen risk of an i metal via an exposure pathway (j), SFij is the slope coefficient for a single element (i) through an exposure pathway (j), and RI is total carcinogen risk.

Results and Discussion

The concentrations of HMs in the 138 soil samples and the background values for the local soil are summarized in Table 2.

As shown in Table 2, the results showed that the contents of heavy metals in soils varied widely. The range of concentration change of Zn, Pb, Cd, Cr, Cu and Mn in the soils of 0~20cm was 964.63-12505.80, 78.10-551.90, 19.40-161.53, 16.18-69.98, 23.73-61.75 and 281.17-338.89 mg/kg, respectively, and the mean concentrations were 4004.94, 225.42, 65.15, 34.69, 44.08 and 313.86 mg/kg, respectively. The ranges of Zn, Pb, Cd, Cr, Cu and Mn in the soils of 20~40cm were 25.10-1160.30, 28.88-89.45, 1.83-17.48, 11.38-69.28, 22.88-52.13 and 256.02-327.31 mg/kg, respectively, and the mean concentrations were 409.70, 48.18, 6.38, 34.84, 31.90 and 285.41 mg/kg, respectively. They were 74.68-484.73, 21.20-62.23, 1.55-7.25, 22.65-3.50, 20.08-47.10 and 276.53-343.77 mg/kg in the soils of 20~40 cm, and the mean concentrations were 215.27, 38.3, 3.47, 36.02, 28.96 and 299.13 mg/kg, respectively.

Table 2. Descriptive statistics of HMs content in soils.

Depth/cm	Parameters	Pb	Zn	Cd	Cr	Cu	Mn
0-20	Max/mg/kg	551.90	12505.80	161.53	69.98	61.75	338.89
	Min/mg/kg	78.10	964.63	19.40	16.18	23.73	281.17
	Mean/mg/kg	225.42	4004.94	65.15	34.69	44.08	313.86
20-40	Max/mg/kg	89.45	1160.30	17.48	69.28	52.13	327.31
	Min/mg/kg	28.88	125.10	1.83	11.38	22.88	256.02
	Mean/mg/kg	48.18	409.70	6.38	34.84	31.90	285.41
40-60	Max/mg/kg	62.23	484.73	7.25	53.50	47.10	343.77
	Min/mg/kg	21.20	74.68	1.55	22.65	20.08	276.53
	Mean/mg/kg	38.83	215.27	3.47	36.02	28.96	299.13
Background values of Shaanxi		16.30	65.80	0.12	65.70	23.50	557.00
Grade II standards		350	300	0.60	250	100	-

Background value, based on a report on heavy metal content by Xue (1985) in agricultural soils of Guanzhong area , Shannxi Province, China; Grade II standards=the Grade II environmental quality standard for soils in China(GB 15618-1995)

The mean concentrations of Cd, Zn, Pb and Cu were observably higher than the background values of Shaanxi Province, especially for Cd, Zn and Pb, at 0~20 cm, 20~40 cm and 40~60 cm. Furthermore, the mean concentrations, including Cd and Zn at 0~20 cm and 20~40 cm as well as Cd at 40~60 cm, far exceeded the soil environmental standard of National Second Grade (Pb≤350, Zn ≤ 300, Cd ≤ 0.60, Cr ≤ 250, Cu ≤ 100) (GB 15618-1995), especially at 0~20 cm, and other elements did not exceed the soil environmental standard of National Second Grade for each layer. Mn did not exceed the soil environmental standard of National Second Grade and the background values of Shaanxi Province, largely because the average concentration range of Mn in soil of the world varies from 270 mg/kg (in Podzoles) to 525 mg/kg (in Cambisols) (Demková *et al.* 2017). The Cd concentration is very low in natural soil, and being often below 0.1 mg/kg throughout the world (Baize and *Sterckeman et al.* 2001, Demková *et al.* 2017). The background value for Shaanxi Province is below 0.12 mg/kg. The concentration of Cd and Zn exceeded all the low exceeded all the value of environmental standards the soil environmental standard of National Second Grade and the background values of Shaanxi Province at all sampling sites in our study area. The concentration of Cr in soil is generally low in China, whereas the concentration of Cd in soil has been found high in most cities of China (Wei and Yang 2010, Liu *et al.* 2018). But, Cd is one of the most toxic HMs, which can cause negative damange to human health and to the biodiversity and activity of soil microbial communities (Li *et al.* 2017, Demková *et al.* 2017, Fan *et al.* 2019).

For ecological risk assessment, we first calculated the monomial potential ecological risk index (Eri), which is the individual ecological risk factor associated with the contribution of HMs. On the basis of the Eri calculation, we calculated the potential ecological risk (RI). The calculation formula of RI synthetically considers HM toxicity, transfer and transformation of HMs within study areas, sensitivity to HM pollution, and differences in regional background values of HMs to remove the influence of regional differences and sources. The calculated results for Eri and RI are shown in Fig. 2. Based on the above results, the contents of Mn in the soils was low and did not exceed the soil environmental standard of National Second Grade and the background values of Shaanxi Province, indicating no pollution and has thus been chosen as a background element in many studies. Meanwhile Mn will no longer be discussed with regard to the ecological risk assessment and health risk assessment.

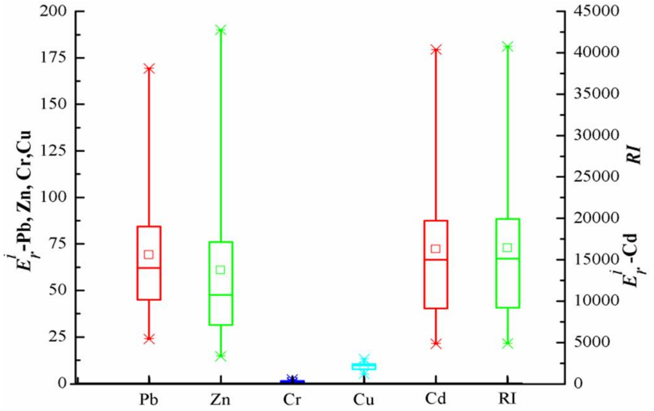

Fig. 2. Spatial distribution of ecological risk for HMs in soil near Pb-Zn Smelter.

Comparing the monomial potential ecological risk index (Eri) (Fig. 2) with its grade classification, the Eri values for Cu and Cr were less than 40, showing a low potential ecological risk overall and that they hardly posed threats in the study area. However, among the five HMs, Cd presented the highest ecological risk as a result of its high toxicity factor, which ranged from 4850.0-40381.25 with a mean value of 16286.81, mainly originated from the smelting activities of the Pb-Zn smelter. Suresh *et al.* (2012) also thought that nonferrous metal mining, refining and manufacture are the main anthropogenic sources of Cd in the environment. In addition, the Eri values of Zn and Pb were in the ranges of 14.66–190.06 and 23.96–169.29, respectively, between low risk and high risk. Overall, the individual potential risk for the average Eri for the HMs is Cd > Zn ≥ Pb > Cu > Cr. Additionally, the calculated RI values ranged from 4902.29 to 40753.80 with an average value of 16427.25, indicating a very high potential ecological risk primarily caused by Cd, Zn and Pb. In particular, there is a risk from Cd because of its high ecological toxicity. Therefore, this may require further attention when considering environmental remediation activities.

Furthermore, the spatial distribution of ecological risk for heavy metals is shown in Fig. 3. The spatial distribution characteristics of Eri and RI for Pb, Zn, Cd and Cu were consistent, which showed a high ecological risk overall in the entire study area and the highest near the smelter chimneys in the southeast and downwind of the smelter in the north. This indicates that the enrichment of metal concentrations caused by smelting activities poses some threat to the ecological environment. Additionally, Cr was a low ecological risk overall the entire study area, the spatial distribution pattern of Cr was different from the other tested metals, and the hot-spot areas of Cr were in the southeast part of the study region.

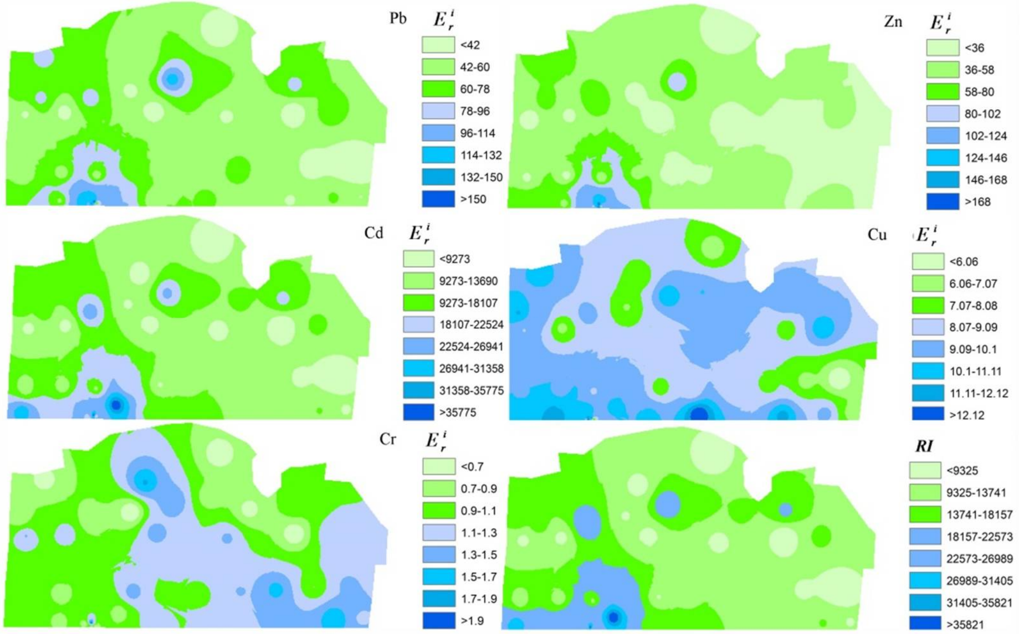

Fig. 3. Spatial distribution of ecological risk for HMs in soil near Pb-Zn Smelter.

The average daily dose (ADD) of heavy metals via several pathways for children and adults from the soil near the Pb-Zn smelter are listed in Table 3.

Table 3. Daily dose of soil HMs in three models.

Elements	statistical	Children			Adults		
	metrics	ADDing	ADDinh	ADDdermal	ADDing	ADDinh	ADDdermal
Pb	Max	7.06×10^{0}	5.19×10^{-9}	1.98×10^{1}	7.56×10^{-1}	5.56×10^{-10}	7.54×10^{-1}
	Min	9.99×10^{-1}	7.34×10^{-10}	2.80×10^{0}	1.07×10^{-1}	7.87×10^{-11}	1.07×10^{-1}
	Mean	2.88×10^{0}	2.12×10^{-9}	8.07×10^{0}	3.09×10^{-1}	2.27×10^{-10}	3.08×10^{-1}
Zn	Max	1.60×10^{2}	1.18×10^{-7}	4.48×10^{2}	7.99×10^{1}	5.88×10^{-8}	1.71×10^{1}
	Min	1.23×10^{1}	9.07×10^{-9}	3.45×10^{1}	6.17×10^{0}	4.53×10^{-9}	1.32×10^{0}
	Mean	5.12×10^{1}	3.77×10^{-8}	1.43×10^{2}	2.56×10^{1}	1.88×10^{-8}	5.47×10^{0}
Cd	Max	7.08×10^{-1}	5.21×10^{-10}	1.98×10^{1}	1.90×10^{-2}	1.39×10^{-11}	7.57×10^{-2}
	Min	8.50×10^{-2}	6.25×10^{-11}	2.38×10^{-1}	2.28×10^{-3}	1.67×10^{-12}	9.09×10^{-3}
	Mean	2.86×10^{-1}	2.10×10^{-10}	8.00×10^{-1}	7.65×10^{-3}	5.62×10^{-12}	3.05×10^{-2}
Cr	Max	3.07×10^{-1}	2.26×10^{-10}	8.59×10^{-1}	8.22×10^{-3}	6.04×10^{-12}	3.28×10^{-2}
	Min	7.09×10^{-2}	5.21×10^{-11}	1.99×10^{-1}	1.90×10^{-3}	1.40×10^{-12}	7.58×10^{-3}
	Mean	1.52×10^{-1}	1.12×10^{-10}	4.26×10^{-1}	4.07×10^{-3}	3.00×10^{-12}	1.63×10^{-2}
Cu	Max	7.89×10^{-1}	5.81×10^{-10}	2.21×10^{0}	8.46×10^{-2}	6.22×10^{-11}	8.44×10^{-2}
	Min	3.03×10^{-1}	2.23×10^{-10}	8.49×10^{-1}	3.25×10^{-2}	2.39×10^{-11}	3.24×10^{-2}
	Mean	5.64×10^{-1}	4.14×10^{-10}	1.58×10^{0}	6.04×10^{-2}	4.44×10^{-11}	6.02×10^{-2}

As outlined in Table 3, the average daily exposure intake of Pb, Zn, Cd, Cr and Cu in topsoil near the Pb-Zn smelter was as follows: for children, the exposure dose (ADDing / ADDinh / ADDdermal) ranges for Pb, Zn, Cd, Cr and Cu were 9.99×10-1-7.06×100/7.34×10-10-5.19×10-9/2.80 × 100-1.98×101,1.23×101-1.60×102/9.07×10-9-1.18×10-7/3.45×101-4.48×102,8.50×10-2-7.08 × 10-1/6.25×10-11-5.21×10-10/2.38×10-1-1.98×101,7.09×10-2-3.07×10-1/5.21×10-11-2.26 × 10-10/1.99×10-1-8.59×10-1,and3.03×10-1-7.89×10-1/2.23×10-10-5.81×10-10/8.49×10-1-2.21 × 100, respectively; for adults, the ranges were 1.07×10-1-7.56×10-1/7.87×10-11-5.56×10-10/1.07 × 10-1-7.54×10-1, 6.17 × 100-7.99 × 101/4.53 × 10-9-5.88 × 10-8/1.32 × 100-1.71×101,2.28×10-3-1.90 × 10-2/1.67×10-12-1.39×10-11/9.09×10-3-7.57×10-2,1.90×10-3-8.22×10-3/1.40×10-12-6.04 × 10-12/7.58×10-3-3.28×10-2, and 3.25×10-2-8.46×10-2/2.39×10-11- 6.22×10-11/3.24×10-2-8.44×10-2, respectively. Thus, the average daily dose of HMs for the children was significantly higher than that of adults for all five metals, which was similar to the study of Xiao et al. (2017). Thus, considerable attention should be paid to the risk exposure for children in daily life. Additionally, the ADDs for different exposure routes for children and adults were different: the ADD of Pb, Zn, Cd, Cr and Cu for children decreased in the order of dermal contact > ingestion > inhalation with dermal contact and ingestion playing the most important roles for children; however, the average daily intake of Pb, Zn and Cu for adults decreased in the order of ingestion > dermal contact > inhalation, and Cd and Cr decreased in the order of dermal contact > ingestion > inhalation. This result is in accordance with the true circumstances. For children, dermal contact is the main exposure pathway for Pb, Zn, Cd, Cr and Cu. In contrast, for adults, ingestion is the main exposure pathway for Pb, Zn and Cu; however, dermal contact is a more common exposure pathway for Cd and Cr. Analogously, Li et al. (2014) also deemed that dermal absorption is the main exposure pathway for Cd and Cr, whereas ingestion is a more common exposure pathway for Pb and Zn. Furthermore, the average daily intake of each toxic metal for children and adults via the three exposure routes followed the descending order of Zn > Pb > Cu > Cd > Cr.

Too much exposure to elevated heavy metals has non-carcinogenic effects on human health. The HQ values for different population groups vary, as shown in Table 4.

Table 4. Hazard quotients of soil HMs for children and adults.

Metals	Statistical metrics	Children				Adults			
		HQ_{ing}	HQ_{inh}	HQ_{dermal}	HQ	HQ_{ing}	HQ_{inh}	HQ_{dermal}	HQ
Pb	Max	2.02×10^{-3}	1.47×10^{-12}	3.76×10^{-4}	2.39×10^{-3}	2.16×10^{-4}	1.58×10^{-13}	1.44×10^{-5}	2.30×10^{-4}
	Min	2.85×10^{-4}	2.09×10^{-13}	5.33×10^{-5}	3.39×10^{-4}	3.06×10^{-5}	2.23×10^{-14}	2.03×10^{-6}	3.26×10^{-5}
	Mean	8.23×10^{-4}	6.02×10^{-13}	1.54×10^{-14}	9.77×10^{-4}	8.82×10^{-5}	6.45×10^{-14}	5.87×10^{-6}	9.41×10^{-5}
Zn	Max	5.33×10^{2}	3.92×10^{-7}	7.46×10^{3}	7.99×10^{3}	2.66×10^{2}	1.96×10^{-7}	2.85×10^{2}	5.51×10^{2}
	Min	4.11×10^{1}	3.02×10^{-8}	5.76×10^{2}	6.17×10^{2}	2.06×10^{1}	1.51×10^{-8}	2.20×10^{1}	4.25×10^{1}
	Mean	1.71×10^{2}	1.26×10^{-7}	2.39×10^{3}	2.56×10^{3}	8.53×10^{1}	6.28×10^{-8}	9.12×10^{1}	1.77×10^{2}
Cd	Max	7.08×10^{-4}	5.21×10^{-13}	1.98×10^{-5}	7.28×10^{-4}	1.90×10^{-5}	1.39×10^{-14}	7.57×10^{-7}	1.97×10^{-5}
	Min	8.50×10^{-5}	6.25×10^{-14}	2.38×10^{-6}	8.74×10^{-5}	2.28×10^{-6}	1.67×10^{-15}	9.09×10^{-8}	2.37×10^{-6}
	Mean	2.86×10^{-4}	2.10×10^{-13}	8.00×10^{-6}	2.94×10^{-4}	7.65×10^{-6}	5.62×10^{-15}	3.05×10^{-7}	7.95×10^{-6}
Cr	Max	1.02×10^{-4}	7.91×10^{-16}	1.43×10^{-6}	1.04×10^{-4}	2.74×10^{-6}	2.12×10^{-17}	5.46×10^{-8}	2.79×10^{-6}
	Min	2.36×10^{-5}	1.83×10^{-16}	3.31×10^{-7}	2.40×10^{-5}	6.33×10^{-7}	4.9×10^{-18}	1.26×10^{-8}	6.46×10^{-7}
	Mean	5.07×10^{-5}	3.92×10^{-16}	7.10×10^{-7}	5.14×10^{-5}	1.36×10^{-6}	1.05×10^{-17}	2.71×10^{-8}	1.38×10^{-6}
Cu	Max	1.97×10^{-3}	1.44×10^{-12}	1.84×10^{-2}	2.04×10^{-2}	2.11×10^{-4}	1.55×10^{-13}	7.03×10^{-4}	9.15×10^{-4}
	Min	7.58×10^{-4}	5.55×10^{-13}	7.08×10^{-3}	7.84×10^{-3}	8.13×10^{-5}	5.94×10^{-14}	2.70×10^{-4}	3.51×10^{-4}
	Mean	1.41×10^{-3}	1.03×10^{-12}	1.31×10^{-2}	1.46×10^{-2}	1.51×10^{-4}	1.1×10^{-13}	5.02×10^{-4}	6.53×10^{-4}

The HQ values for Pb, Cd, Cr and Cu for adults and children via the different pathways were less than 1, and the total HQ values via the three pathways were less than 1 (Table 4). The HQ values for Zn via ingestion (HQing) and dermal contact (HQdermal) and the total HQ values were greater than 1. These results illustrated that Cd, Pb, Cu and Cr had no possibility of adverse health effects for exposed populations (adults and children). However, Zn showed possible adverse health effects, and for children, it was greater than adults; thus, the risk of non-carcinogenic exposure for children cannot be ignored; however, it should not be exaggerated. In addition, according to the HQ values, it was obvious that children tended to have a higher probability than adults, indicating that children are more susceptible to environmental contaminants, which may be due to the behavioral and physiological characteristics of children. The HQ values of different heavy metals for children and adults was in the order of Zn> Cu > Pb > Cd> Cr. The HQ values for the three exposure pathways for children decreased in the following order: for Pb, ingestion > inhalation > dermal contact; for Zn and Cu, dermal contact > ingestion > inhalation; for Cd and Cr, ingestion > dermal contact > inhalation. For adults, the HQ values decreased in the following order: for Zn and Cu, dermal contact > ingestion > inhalation; for Pb, Cd and Cr, ingestion > dermal contact > inhalation. These results are likely due to the fact that children are more likely to contact heavy metals via inadvertent ingestion, such as via pica behavior, hand or finger sucking, or outdoor play activities (Mielk *et al.* 1999, Karim and Qureshi 2014, Han *et al.* 2018).

According to the results of the non-carcinogenic risk assessment, the hazard indices for exposed populations are shown in Figs 4-5.

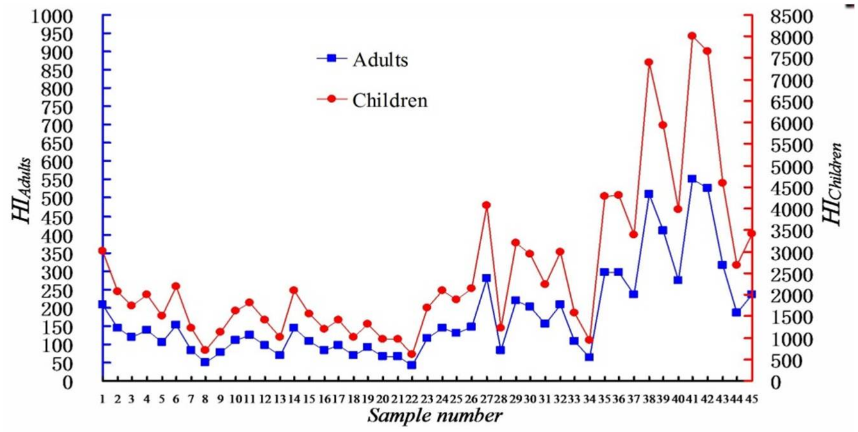

Fig. 4. The distribution map of hazard index (HI) in adults and children.

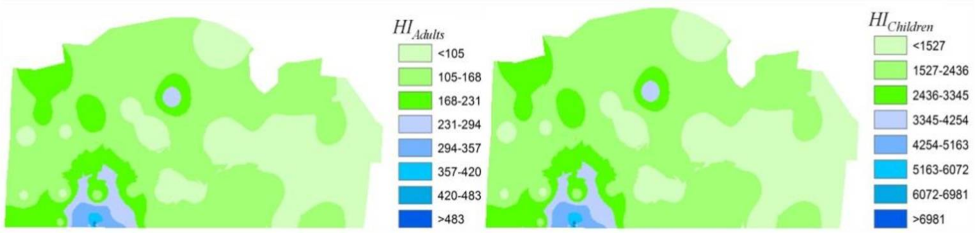

Fig. 5. The distribution pattern of hazard index (HI) for adults and children.

As shown in Fig. 4, the calculated HI values for children ranged from 616.67 to 7994.60, and the average was 256.25; for adults, the calculated HI values ranged from 42.52 to 551.29, and the average was 176.55. Obviously (Fig. 5), for adults and children, the HI values for the five metals from all soil samples far exceeded the safe levels (=1), suggesting that adults and children are exposed to significant non-carcinogenic health risks, which should be addressed and studied in more detail. Additionally, children have higher health risks that are non-carcinogenic compared with adults based on their higher calculated HI values, indicating that children are exposed to a significant non-carcinogenic risk due to their behavioral and physiological characteristics, especially hand-to-mouth transfer of soil. Similar results have also been observed in other studies (Li *et al.* 2014, Tepanosyan *et al.* 2017, Xiao *et al.* 2017, Han *et al.* 2018). The accumulation of Zn is the main cause of the non-carcinogenic risk based on their high HQ values, and excessive intake of Zn leads to chronic diseases that affect the healing of wounds, the immune system response, the ability to taste and smell and stunted growth (Steffan *et al.* 2018). Thus, the risks for people, and especially children, from exposure to multiple metals in the soil from the Pb/Zn smelter require considerable attention. Zn should be regarded as a priority control pollutant, although the results may not reveal that people actually experience adverse health effects.

Although the five metals in this study have chronic non-carcinogenic health risks, only two metals (Cd and Cr) have a carcinogenic risk, and the carcinogenic risks for Cd and Cr were considered only via inhalation, as shown in Figs 6-7.

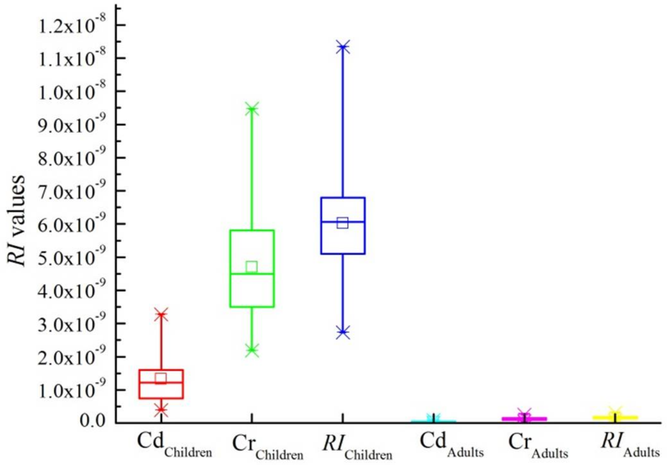

Fig. 6. Boxplots of carcinogenic risks of Cd and Cr for children and adults.

For the carcinogenic risk (Fig. 6), the single carcinogenic risk values for Cd and Cr for children were in the ranges of 3.94×10-10 - 3.28×10-9 and 2.19×10−9 - 9.47×10−9 with means of 1.32×10-9 and 4.07×10−9, respectively; the single carcinogenic risk values for Cd and Cr for adults were in the ranges of 1.06×10-11 - 8.79×10−11 and 5.87×10-11 - 2.54×10−10 with means of 3.54×10-11 and 1.26×10−10, respectively. The total carcinogen risk values (RI) for children and adults were in the ranges of 2.74×10-9 - 1.13×10-8 and 7.33×10-11 - 3.04×10-10, respectively. These results show that all the carcinogenic risk values for the two population groups were less than 10-6 overall in the entire study area (Fig.7), which is not considered to pose significant health effects. Thus, children and adults faced an acceptable carcinogenic risk. In addition, the carcinogenic risk levels for children were higher than those for adults, and the carcinogenic risks for the two population groups showed that Cr posed a higher risk than Cd. Overall, the cancer risk for all HMs in this study were within the acceptable range, implying negligible carcinogenic risk; however, more attention needs to be given to this health issue.

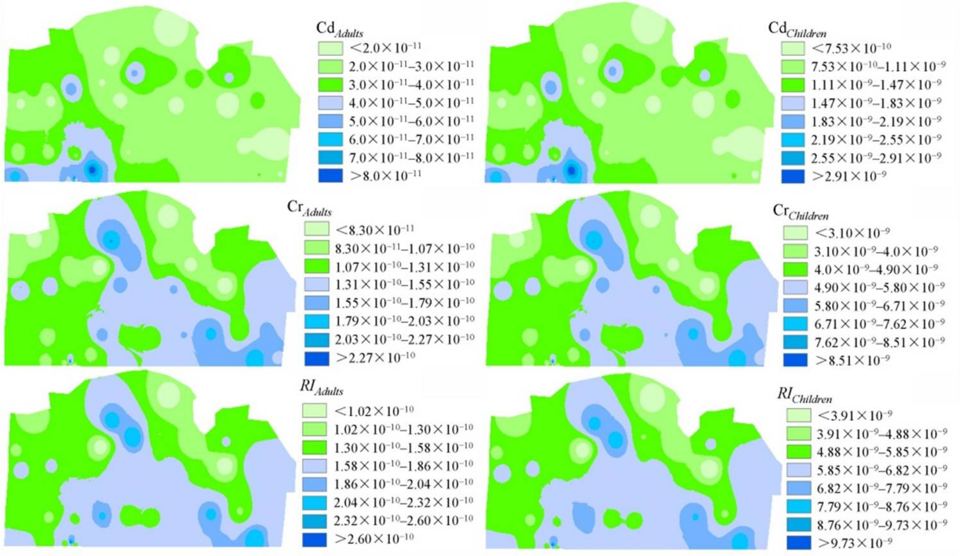

Fig. 7. Spatial distribution maps of carcinogenic risks of Cd and Cr for children and adults.

A total of 138 samples were collected from near the Pb-Zn smelter in 2017. The concentrations of six potentially toxic HMs elements (Pb, Zn, Cd, Cu, Cr and Mn) in the soil near the Pb-Zn smelter were determined by using an air-acetylene flame atomic absorption spectrophotometer (SHIMADZU AA-6800). The pollution characteristics of the HMs were statistically analyzed by using a mathematical statistics method. The pollution levels were assessed using the potential ecological risk index (RI). The health risk upon exposure to soil HMs was assessed for children and adults using the health risk assessment model developed by the USEPA.

The results showed the following: (1) The mean concentrations of Pb, Zn, Cd and Cu, excluding Mn and Cr, were significantly higher than the background values of Shaanxi Province ; the mean concentrations for Cd and Zn at 0~20 cm ,20~40 cm,40~60 cm, far exceeded the soil environmental standard of National Second Grade, indicating that Zn, Cd, Pb and Cu pollution in soil around the smelter pollution is very serious, especially in the topsoil (0~20 cm).

(2) The ecological risk assessment indicated the following. For Cu and Cr, there was an overall low potential ecological risk, whereas for Cd, the ecological risk was the highest. For Zn and Pb, it was between low risk and high risk. The RI results exhibited a very high potential ecological risk, mainly caused by Cd, Zn and Pb, especially Cd. The spatial distribution of Eri for Pb, Zn, Cd and Cu and the RI showed a high ecological risk overall for the entire study area, which was the highest near the smelter chimneys in the southeast and downwind of the smelter in the north. Cr was lowest overall ecological risk in the entire study area.

(3) The health risk analysis showed that dermal contact was the dominant exposure pathway for Zn, Pb, Cd, Cr and Cu for children, and for adults, ingestion was the main exposure pathway for Zn, Pb and Cu.

The HQ values showed that Pb, Cd, Cr and Cu exhibited no possibility of adverse health effects for the exposed populations (adults and children), but Zn exhibited possible adverse health effects. The HI values for Pb, Zn, Cd, Cr and Cu from all soil samples far exceeded the safe levels (=1), suggesting that adults and children are exposed to significant non-carcinogenic health risks, and children are under higher non-carcinogenic health risks than adults.

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