Environ Monit Assess (2016) 188: 413
DOI 10.1007/s10661-016-5406-0

# Concentrations, spatial distribution, and risk assessment of soil heavy metals in a Zn-Pb mine district in southern China

**Jianying Qi · Hailong Zhang · Xiangping Li · Jian lu · Gaosheng Zhang**

Received: 26 August 2015 / Accepted: 6 June 2016 /

**Abstract** China is one of the largest producers and consumers of lead and zinc in the world. Lead and zinc mining and smelting can release hazardous heavy metals such as Cd, Pb, Zn, and As into soils, exerting health risks to human by chronic exposure. The concentrations of Cd, Zn, Pb, and As in soil samples collected from a Pb-Zn mining area with exploitation history of 60 years were investigated. Health risks of the heavy metals in soil were evaluated using US Environmental Protection Agency (US EPA) recommended method. A geo-statistical technique (Kriging) was used for the interpolation of heavy metals pollution and Hazard Index (HI). The results indicated that the long-term Pb/Zn mining activities caused the serious pollution in the local soil. The concentrations of Cd, As, Pb, and Zn in topsoil were 40.3 ± 6.3, 103.7 ± 37.3, 3518.4 ± 896.1, and 10,413 ± 2973.2 mg/kg dry weight, respectively. The spatial distribution of the four metals possessed similar patterns, with higher concentrations around Aayiken (AYK), Maseka (MSK), and Kuangshan (KS) area and more rapidly dropped concentrations at upwind direction than those at downwind direction. The main pollutions of Cd and Zn were found in the upper 60 cm, the Pb was found in the upper 40 cm, and the As was in the upper 20 cm. The mobility of metals in soil profile of study area was classed as Cd > Zn ≫ Pb > As. Results indicated that there was a higher health risk (child higher than adult) in the study area. Pb contributed to the highest Hazard Quotient (57.0 ~ 73.9 %) for the Hazard Index.

**Keywords** Heavy metals · Health risk assessment · Pb/Zn smelting · Kriging interpolation

## Introduction

Metals such as lead (Pb), zinc (Zn), and cadmium (Cd) generally refer as heavy metals with densities greater than 5 g per cubic centimeter (Oves et al. 2012). Metalloid Arsenic (As) is often categorized as heavy metal (Huamain et al. 1999). These metals are always nonessential and have health risks to human beings. For example, Cd, a toxic and unnecessary element for human body, can have adverse effects such as prostatic proliferative lesions, pulmonary adenocarcinomas, lung cancer, kidney dysfunction, and bone fractures after chronic exposure (Żukowska and Biziuk 2008). Chronic As exposure may lead to hyperkeratosis, skin lesions, and cancer of the skin, lung, bladder, and kidney (Hughes 2002). Lead can cause reversible effects on

J. Qi · H. Zhang
South China Institute of Environmental Science, Ministry of Environmental Protection, Guangzhou 510655, People's Republic of China

X. Li (✉)
School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, People's Republic of China
e-mail: lxping1@sina.com

J. lu · G. Zhang (✉)
Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), 17th Chunhui Road, Yantai, Shandong 264003, People's Republic of China
e-mail: gszhang@yic.ac.cn

the activity of some blood enzymes, the development of the central nervous system and IQ, and even to death if exposure is sufficiently large or protracted (Kaufmann et al. 2003). Actually, blood lead concentrations, even those below 10 μg per deciliter, are inversely associated with children's IQ scores at 3 and 5 years of age, with greater associated declines in IQ at higher concentrations (Canfield et al. 2003). Excessive zinc intake can cause stomach cramps, nausea, and long-term high dose exposure can affect cholesterol balance and even cause infertility although zinc is an essential element (Zhang et al. 2012).

Heavy metal pollution of soils attracted more attentions due to the potential toxicity of metals (Aelion et al. 2008; Li et al. 2014a). Although heavy metals may occur naturally in soils, additional contributions come from anthropogenic activities such as agriculture, urbanization, industrialization, and mining (Anju and Banerjee 2012; Gu et al. 2014). Among them, mining activities and metal smelting are the main sources of hazardous heavy metals (Liu et al. 2014). In fact, mining activities alone have produced about 1,500,000 ha of wasteland in China, increasing at the rate of 46,700 ha per year (Zhuang et al. 2009). The concentrations of the heavy metals in the mine area soil are always much higher than those in the unaffected area. Rodríguez et al. (2009) studied the heavy metals concentrations in soil (pasture land) around an old Spanish Pb-Zn mine and found that the concentrations of Pb, Zn, and Cd were 1505.5, 596.1, and 3.76 mg/kg, respectively. Carla Candeias et al. (2014) investigated the As concentration in the soil of S. Francisco de Assis village which was influenced by the mining activities. They observed that the As content in the rhizosphere soils exceeded 20 times than the reference value of local guideline (11 mg/kg). Similar phenomena were also observed in many mining areas of China. Zhou et al. (2007) studied the soil heavy metal concentration in the vicinity of the Dabaoshan Mine, Guangdong Province, China. They found that the average concentrations of Cu, Zn, Cd, and Pb in the paddy soils (near the mine area) were 561, 1140, 2.48, and 191 mg/kg, respectively, significantly higher ($p \leq 0.05$) than those in control site. Li et al. (2008) analyzed the heavy metals concentrations in Jinding Pb-Zn deposit, Yunnan Province, China and found that the of Cd were abnormally higher (69.5–95.4 mg kg$^{-1}$) with an average value of 83.0 mg kg$^{-1}$ in the center of the mining area than those in the control area (1.64–2.24 mg kg$^{-1}$).

With 60-year exploitation history, mining activities of the Huize Zn-Pb district (it has been proven to reserve about 1.53 million tons of lead-zinc) in north-east of Yunnan Province, P.R. China have played a major role in the development of the non-ferrous industry of China (Han et al. 2007) and generated large quantities of mine waste without any proper treatment. Such long-time, large-scale mining activities have led to the release of Cd, Pb, Zn, and As in large amounts from ores into soils and other supergene environment and may pose a great health risk to the people who live in the surroundings. However, the pollution of the soil by mining activities and its health risk assessment got less attention in this area. Therefore, it is very necessary to determine the heavy metal pollution levels and assess potential health risk in this area. Geographic Information System (GIS) technology which has been extensively applied in pollution studies including those of soil pollution at a regional scale (Ha et al. 2014; Ebbinghaus et al. 1997; Zhang 2006) was used to find the sensitive area in this study.

The main objectives of this study were (1) to determine the concentrations and spatial distribution of Pb, Zn, Cd, and As in the soil of Huize, (2) to evaluate the health risk of adult and children in this area using US EPA health risk assessment model, and (3) to interpolate point patterns of entire study area for obtaining an aerial perspective of the spatial distribution of the contaminants and health risk.

## Experimental section

### Study area

The study area is located at Huize (103° 03′–103° 55′ E, 25° 48′–27° 04′ N), a small town in Yunnan Province, south-west China. The region is rich in lead and zinc resources, and the industry of lead and zinc production in Huize is among the top six in China. Zhehai (ZH, the annual precipitation and main wind direction are 815.8 mm, southeast by east (ESE), respectively) and Kuangshan (KS, the annual precipitation and main wind direction are 839.9 mm, northeast by east (ENE), respectively) were chosen as the study area. Jinzhong (JZ, the annual precipitation and main wind direction are 791.5 mm, northeast by east (ENE), respectively) was chosen as the control area, located at approximately 10 km southwest of Zhehai. Our previous survey showed that Zhehai (population over 90,000) was one of the most seriously polluted towns in Huize and had 32 Pb-Zn-related enterprises. Kuangshan locates in the northeast of the Huize and the population is about 20 thousands in this town. Jinzhong locates in the southwest of the Huize and has no metal pollution-related enterprise. Six villages governed by Zhehai town including Maseka (MSK), Ayiken (AYK), Liushucun (LSC), Gangtiecun (GTC), Xincun (XC), and Wulipai (WLP) were emphasized due to the large variation of the heavy metals concentrations in this town.

## Sample collection and preparation

Soil samples were collected in March 2012. Ninety topsoil samples (0 ~ 20 cm) and five soil profiles (0 ~ 20 cm, 20 ~ 40 cm, 40 ~ 60 cm, 60 ~ 80 cm, and 80 ~ 100 cm, corresponding to ZH-A, ZH-B, ZH-C, ZH-D, and JZ in figures) were collected across the study area (Fig. 1), and the locations of sample sites were recorded using a portable GPS. The soil sampling points were selected on the basis of the distribution of the pollution-related enterprise. To minimize the uncertainty, five subsamples were collected to form a composite soil, transferred to acid-washed dark-colored polyethylene bags, and then transported to the laboratory immediately. Samples were also collected in Jinzhong Town which locates at approximately 10 km southwest of Zhehai Town and has no Pn-Zn-mine and related enterprises.

## Analyses of heavy metals in soil

After picking up the small stones and root from original samples, the soil samples were air-dried and sieved by passing through a <2 mm polyethylene sieve before heavy metal analysis. All glass and Teflon wares used were previously soaked overnight in $HNO_3$ (10 %) and rinsed thoroughly with Milli-Q water. Each sample (0.25 g) for Cd, Zn, and Pb analysis was placed into a pre-cleaned Teflon tube with $HNO_3$ (69 %, 20 ml) and standing overnight. Then the sample was put on the Graphite digester (Perkin Elmer SPB 50-72,USA ) at 100 °C until the liquid did not produce the brown gas with a residual volume about 3 ml. The sample was cooled down and then 2 ml of $HClO_4$, 2 ml of HF, and 5 ml of $HNO_3$ were added and digested at 130 °C until the amount of residual liquid was close to 1 ml. The cooled mixtures were decanted into 100 ml colorimetric tube. The pretreatment method for As was based on the Soil quality-Analysis of total mercury, arsenic, and lead contents-Atomic fluorescence spectrometry-Part 2: Analysis of total arsenic contents in soils (GB/T 22105.2-2008 People's Republic of China National Standard) and measured by Atomic Absorption Spectrophotometer (AAS-PF6, Beijing Purkinje General, detection limit 0.5 mg/kg). Pb, Zn, and Cd were measured with an inductively coupled plasma mass spectrometry (ICP-MS DRC-e, Perkin Elmer, detection limits are 0.2, 0.5, and 0.1 mg/kg, respectively) after the mixture was filtered by 0.45 μm microporous membrane. For quality control, regent blank (3 blanks per 20 samples) and replicates made up 15 %, respectively. The recoveries of standard reference material (GBW(E)70009, GBW(E)700011, GSD-7a (obtained from the National Research Center)) were satisfactory: As (93 ~ 99 %), Pb (101 ~ 104 %), Cd (96 ~ 113.6 %), and Zn (98 ~ 101 % ). In addition, To estimate the pH and organic carbon content of soil samples, five samples were randomly chosen and analyzed by a pH meter (Orion 3-star benchtop pH meter, Thermo Fisher Scientific, USA) and a TOC analyzer (multi N/C 3000, Analyticjena Co. Germany). These samples are weakly acidic, and the pH values range from 5.98 to 6.22. The total organic carbon contents are in the range of 2.43–2.73 %.

## Statistical analysis

An independent sample *t* test on the concentrations in soil was used to determine the difference between study area and control area with SPSS version 20 software. A $p < 0.05$ was taken to indicate statistical significance.

## Risk assessment

Residents living in mention area are potential receptors of the heavy metal in topsoil. Exposure to metal-contaminated soil is always via three paths including direct inhalation of soil by mouth and nose, dermal adsorption of soil adhered to exposure skin, and ingestion (especially for children since their deliberate hand-to-mouth movements). In fact, exposure through dermal adsorption and ingestion always play the most important role among the exposure pathways (Qu et al. 2012; Li et al. 2014b). The direct inhalation exposure through mouth and nose always can be ignored (Zheng et al. 2010) because of the lower hazard quotient. Therefore, only the dermal adsorption and ingestion exposure were considered in this study. The health risk of soil in the study

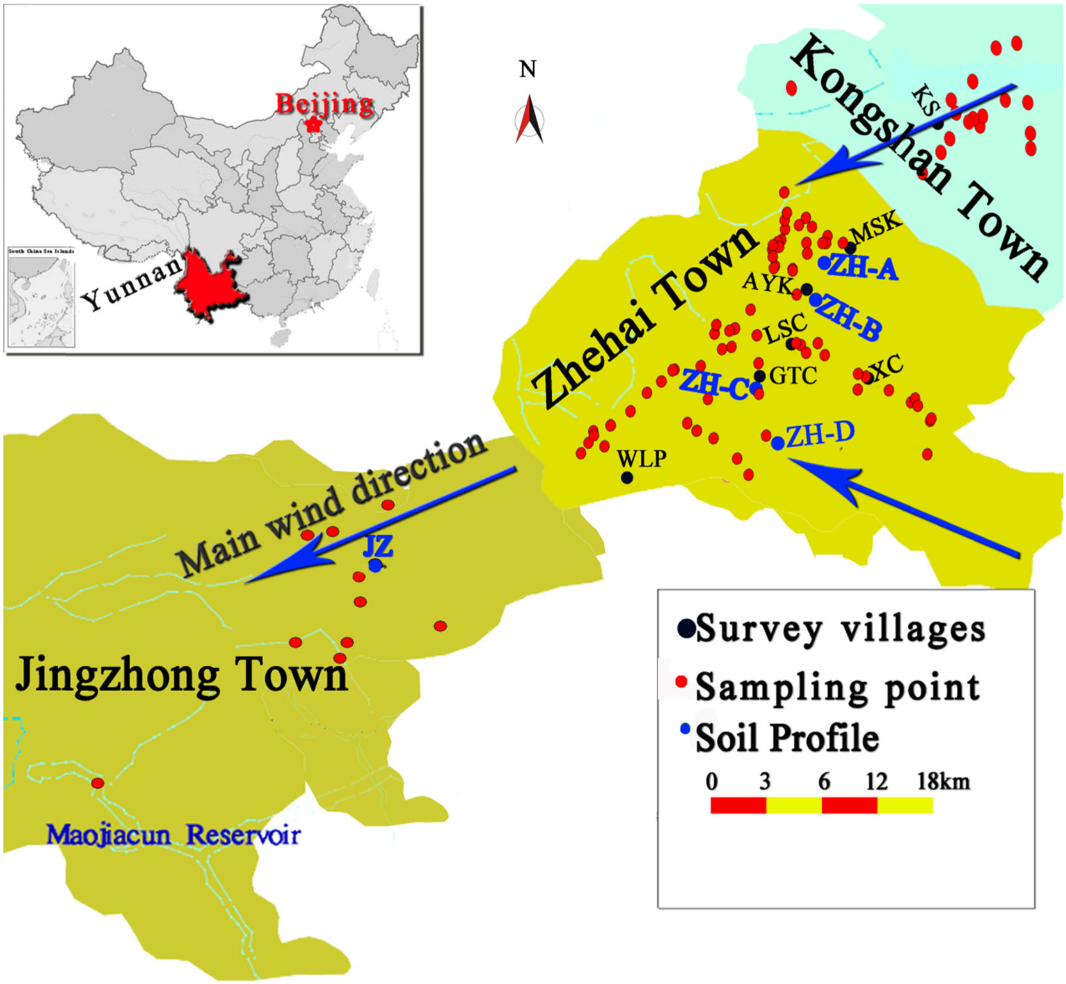

**Fig. 1** Sampling locations of topsoil and soil profile (*created by Map-Gis 6.7 program*)

area was calculated based on the human health evaluation manual (part A) and supplemental guidance for dermal risk assessment (part E). The chemical daily intake (CDI) and dermal adsorption dose (DAD) were estimated to assess the risks posed by heavy metals in soil via ingestion and dermal contact. The equations were as follows:

$$\mathrm{CDI}_{\mathrm{ingest}} = \frac{\mathrm{C} \times \mathrm{IngR}}{\mathrm{BW}} \times \frac{\mathrm{EF} \times \mathrm{ED}}{\mathrm{AT}} \times \mathrm{CF} \qquad (1)$$

$$\mathrm{DAD}_{\mathrm{dermal}} = \frac{\mathrm{C} \times \mathrm{SA} \times \mathrm{AF} \times \mathrm{ABS}}{\mathrm{BW}} \times \frac{\mathrm{EF} \times \mathrm{ED}}{\mathrm{AT}} \times \mathrm{CF} \qquad (2)$$

where C is the heavy metal concentration (mg/kg) in soil; IngR is the ingestion rate (according to US EPA model, 200 mg day$^{-1}$ for children and 100 mg day$^{-1}$ for adult); EF is the exposure frequency, equaling to 350 days year$^{-1}$ (U.S. EPA 2002); ED is the exposure duration (6 years for children and 24 years for adults); BW is the average body weight (60 kg for adult and 15 kg for child (Lee et al. 1994)); AT = ED × 365 days; CF is the conversion factor (10$^{-6}$ kg mg$^{-1}$); SA is the surface area of the skin that contacts the soil (5700 cm$^2$ for adults and 2800 cm$^2$ for the children); AF is the skin-soil adherence factor (0.2 mg cm$^{-2}$ for both adult and children); ABS is the dermal absorption factor 21 (0.03 for As, 0.001 for Cd, Zn and 0.1 for Pb) (U.S. EPA 2012).

The upper limit of the 95 % confidence interval for the mean (95 % UCL (upper confidence limit)) was used to represent the "reasonable maximum exposure" in exposure assessment of this study. The 95 % UCL of the arithmetic mean of contents of heavy metals was calculated using the following formula:

$$95\ \%\ \mathrm{CI} = \mathrm{EXP}\left\{\mathrm{X} + 0.5 \times \mathrm{S}^2 + \frac{\mathrm{s} \times \mathrm{H}}{\sqrt{\mathrm{n}-1}}\right\} \tag{3}$$

where "X" is the arithmetic mean of the log-transformed data; "s" represents the standards deviation of the log-transformed data; "H" is the H-statistic (Gilbert 1987); "n" is the number of samples. Hazard quotient (HQ) means the non-carcinogenic risks of single contaminant. Hazard index (HI) represents the total non-carcinogenic risks of different pollutants through the ingestion and dermal absorbed exposure ways. The exposure risk of soil through ingestion and dermal contact was calculated by the equations as follows:

$$\mathrm{HQ} = \frac{\mathrm{CDI}}{\mathrm{RfDo}} = \frac{\mathrm{DAD}}{\mathrm{RfDo} \times \mathrm{GIABS}} \tag{4}$$

$$\mathrm{HI} = \sum \mathrm{HQ_i} \tag{5}$$

where RfDo is the oral reference dose (mg $\mathrm{kg}^{-1}$ $\mathrm{day}^{-1}$), and it is the estimated daily exposure to the human population that is likely not to have an appreciable risk of deleterious effects during a life time (RfDo for As, Cd, Pb, and Zn (U.S. EPA 2012) are $3.0 \times 10^{-4}$, for $1.0 \times 10^{-3}$, $3.5 \times 10^{-3}$, and 0.3, respectively). As a result of this, $\mathrm{HQ} \leq 1$ means that unlikely adverse health effects whereas $\mathrm{HQ} > 1$ suggests the probability of the adverse health effects. An $\mathrm{HQ} > 10$ is considered to be high chronic risk (Leung et al. 2008). GIABS is gastrointestinal absorption factor (U.S. EPA 2012) (1 for As, Pb, Zn, 0.025 for Cd).

## Results and discussion

### Heavy metal concentrations in topsoil

Heavy metal concentrations in topsoil from AYK, MSK, LSC, GTC, WLP, XC, KS, and control area JZ were showed in Fig. 2. The Cd concentration ranged from 3.06 to 40.3 mg/kg in the study area, which exceeded the limit of Chinese grade III guideline by 2.06 ~ 39.3 times. Cd concentrations in AYK, MSK, and XC were higher than those in other sites, with values of 40.3 ± 6.3, 20.5 ± 5.7, and 9.22 ± 6.4 mg/kg, respectively. Actually, our survey showed that there were 29 enterprises (related with Pb and Zn) in Zhelai Town, three enterprises in Kuangshan Town, and no enterprise in the Jinzhong of the study area. About 20 enterprises were distributed in AYK and MSK, two small villages belonging to Zhehai Town. The Cd concentration in WLP where was furthest from enterprises was 3.13 ± 2.5 mg/kg, which was the lowest value in the study area. In previous studies, Navarro et al. (2008) reported concentrations (in the Spain la, an abandoned Pb-Zn mine area soils) of 41 mg/kg and similar concentrations have been got in other areas (Pruvot et al. 2006; Jung and Thornton 1996). The concentration of Cd in JZ (the control area) was 0.67 ± 0.14 mg/kg and significantly lower ($p < 0.05$) than those of the studied areas. The concentrations were close to those of the less polluted community (Ha et al. 2014) or urban areas (Ordóñez et al. 2003).

Concentrations of As ranged from 10.4 to 103.7 mg/kg in the study area. And the As concentrations in the AYK, MSK, and KS were 103.7 ± 37.3, 91.6 ± 21.9, and 45.71 ± 12.0 mg/kg, respectively, and exceeded the Chinese grade III guideline (40 mg/kg), also higher than those in Avile's (N. Spain), an industrial city with a Zn smelter located in the north (Ordóñez et al. 2003), but lower than the result (584 mg/kg, soil from a farmland spilled by Pb-Zn mine in Hunan province, China) reported by Liu et al. (2005). The concentration of As in the control area was 3.15 ± 0.4 mg/kg, lower than the Chinese grade I (natural background was 15 mg/kg). The concentrations of As in MSK, AYK, LSC, GTC, XC, and KS were significantly higher ($p < 0.05$) than those of the control area sites JZ. And there were not significantly difference between the As concentrations in soils of WLP and JZ.

Figure 2b showed the Zn and Pb concentrations in the topsoil of AYK, MSK, LSC, GTC, WLP, XC, KS, and control area JZ. The Pb concentration ranged from 128.7 to 3518.4 mg/kg. The concentration of Pb in AYK, MSK, and KS were 3518.4 ± 896.1, 2237.6 ± 463.3, and 1430.1 ± 435.1 mg/kg, respectively, and exceeded the Chinese grade III guideline (500 mg/kg for Pb) by 5.0, 2.5, and 0.9 times. The Pb concentration in the control area was 49.26 mg/kg, which was lower than the Chinese grade II guideline (300 mg/kg). The concentrations of Pb in MSK, AYK, LSC, GTC, XC, and KS were significantly higher ($p < 0.05$) than those of the control area sites JZ. Similar to arsenic, there was no significant difference between the Pb concentration in topsoil of WLP and JZ. The Zn concentration ranged from 604.6 to 10,413 mg/kg

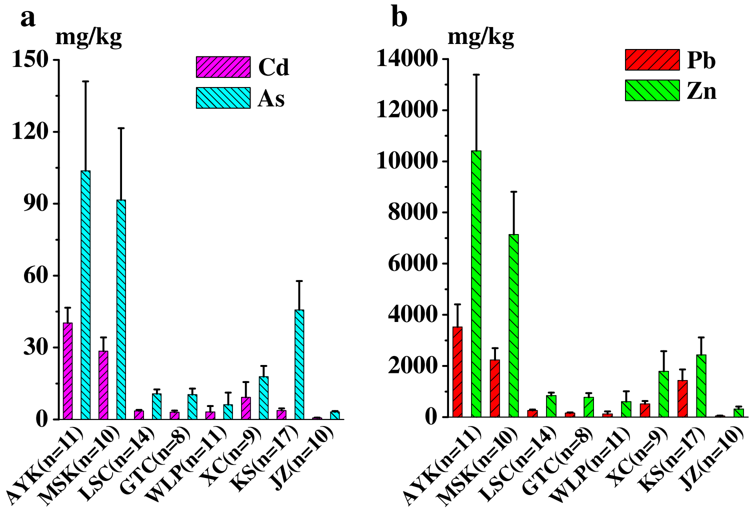

**Fig. 2** Cd, As (**a**) and Pb, Zn (**b**) concentrations (mean) of topsoil samples (<2 mm) (*Created by Origin 8 program*)

and exceeded the Chinese grade III guideline (500 mg/kg for Zn) by 0.2 ~ 19.8 times. The Zn concentration in the control area was 321.1 ± 89.0 mg/kg and lower than the Chinese grade III guideline. The concentrations of Zn in MSK, AYK, LSC, XC, GTC, and KS were significantly higher ($p < 0.05$) than those of the control area sites JZ. There was no significant difference of the Zn concentration in WLP topsoil compared with control area sites topsoil.

In general, the concentration of Cd, Pb, Zn, and As in the study area was higher than those in the control area. The concentration of heavy metal and As in AYK, MSK, and KS was higher than those of other villages, indicating that the smelt activities make main contribution to the high concentration of heavy metal in the topsoil. This is in agreement with previous studies (Li et al. 2015; Zhao et al. 2012).

## Spatial distribution of heavy metals in topsoil

Geo-statistical Analysis Kriging was applied to interpolate the concentration of topsoil samples in order to gain an aerial perspective of the spatial distribution of the heavy metals through the software Map GIS6.7. Figure 3 illustrated the heavy metals and As distribution. The spatial patterns of the four metals were similar in the study area, with higher concentrations around AYK, MSK, and KS area. The concentrations of Cd, As, Pb, and Zn in the topsoil decreased significantly with distances away from the AYK, MSK, and KS area. Since the main wind direction was ESE and ENE in the ZH and KS, respectively, the Cd, As, Pb, and Zn in the topsoil decreased more rapidly in the ESE (upwind direction) and ENE in the ZH and KS than those in the downwind direction, respectively. The previous studies also obtained the similar distribution of metals concentrations nearby smelter areas. Li et al. (2011) found the metal concentrations in soils near a Pb/Zn smelter in east Hunan province, China decreased with increasing distance from the smelter in the dominant wind direction. Bi et al. (2006) reported the heavy metals (Zn, Pb, and Cd) concentrations in the topsoil of a zinc smelting areas in Hezhang County, western Guizhou, China dropped more rapidly at upwind direction than those at downwind direction. Therefore, the observed trend of metal distribution in topsoil could be mainly related by smelter dust emissions.

## Heavy metals distribution on the soil profile

Four soil profiles (ZH-A, B, C, and D) were collected from Zhehai town, where was seriously contaminated with heavy metals. In addition, a control soil profile sample was collected from Jinzhou town. These soil samples were analyzed for metals. Figure 4 demonstrated the soil content and the distribution of the different heavy metals vs. depth. Obviously, the As, Pb, Cd, and Zn concentrations in soil profile samples from Jinzhou town were very low (below the Grade II of the Chinese Environmental standard quality for soils), indicating that they were not contaminated by anthropogenic heavy metals. In general, the concentration of Cd, Pb, Zn, and As changed significantly in the 0 ~ 60 cm depth range for profiles of ZH-A and ZH-B, changed slightly for the whole soil profile of ZH-C, and changed

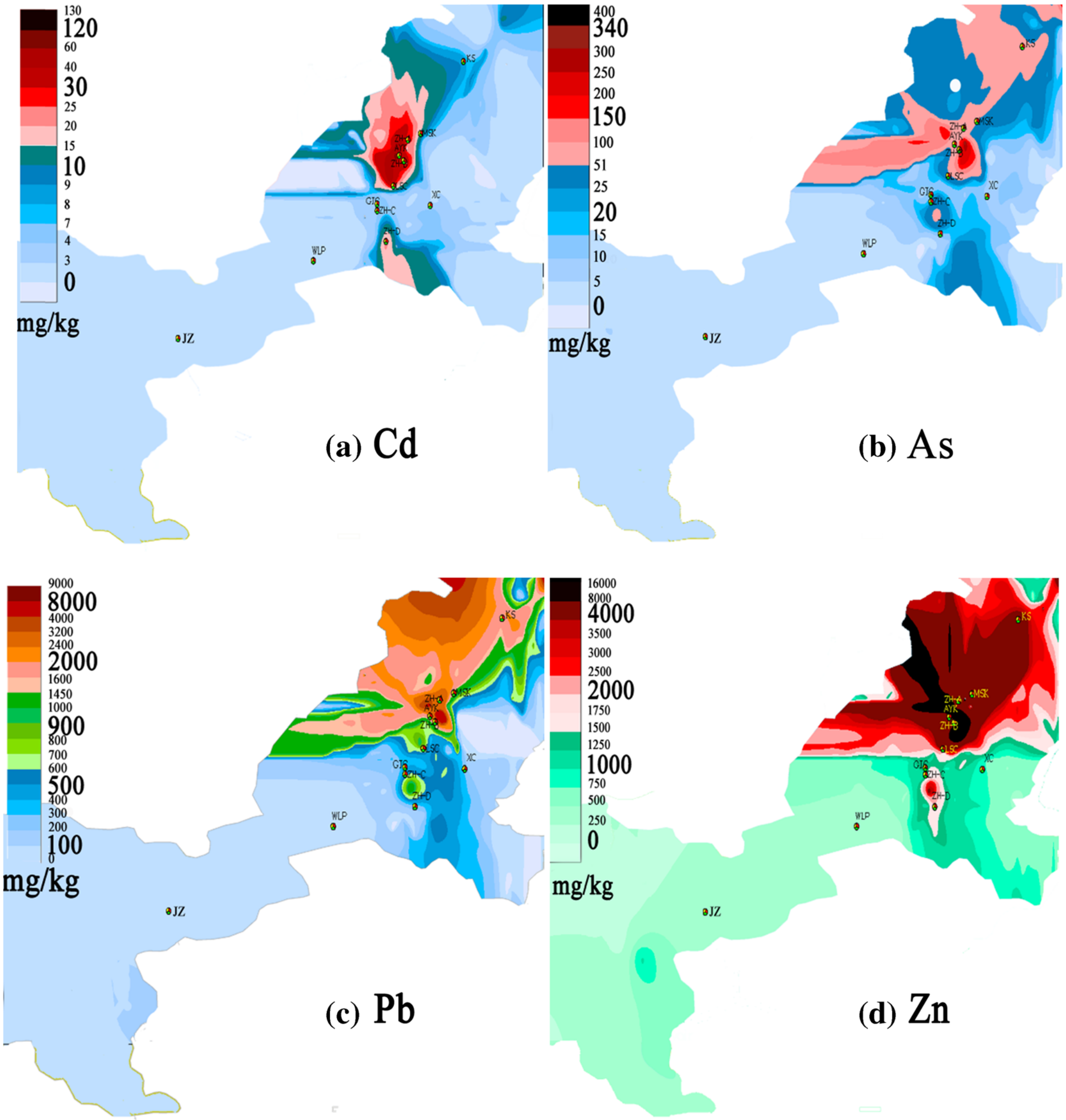

**Fig. 3** Spatial distribution maps of Cd (**a**), As (**b**), Pb (**c**), and Zn (**d**) in top soil in the survey area (*created by Map-Gis 6.7 program*)

significantly in the 0 ~ 40 cm depth range for the profile of ZH-D. The majority of Pb pollution of soil samples from ZH-A and ZH-B was found at the upper 0 ~ 40 cm. With an increase in the depth, the Pb content decreased and reached the control area level at a depth of about 60 cm. Similarly, the Zn and Cd also showed an abrupt decreasing trend. However, their pollution reached a depth of more than 60 cm for Zn and 100 cm for Cd (ZH-B). The results indicated stronger mobility of Zn and Cd than that of Pb. Based on these results, we can classify the mobility of these metals in the following order: Cd > Zn ≫ Pb. For profiles of ZH-A and ZH-B, the concentration of arsenic dropped sharply with an increase in the depth in the upper 0 ~ 20 cm. For other two profiles, it decreased slightly. Obviously, the mobility of arsenic was lower than that of Zn, Pb, and Cd. In fact, the chemical forms of Cd, Pb, Zn, and As in the soil affected their mobility. Krysiak and Karczewska (2007) made a sequential extraction in a mining and processing areas and found that the arsenic in soils was relatively strong bond, possibly to Fe and Al oxides. Therefore, the contributions of potentially mobile arsenic were relatively low. The mobility of metals in soil profiles was classed as Cd > Zn ≫ Pb > As. In contrast with arsenic, Cd and Zn were usually associated with the more liable fractions such as carbonate minerals since

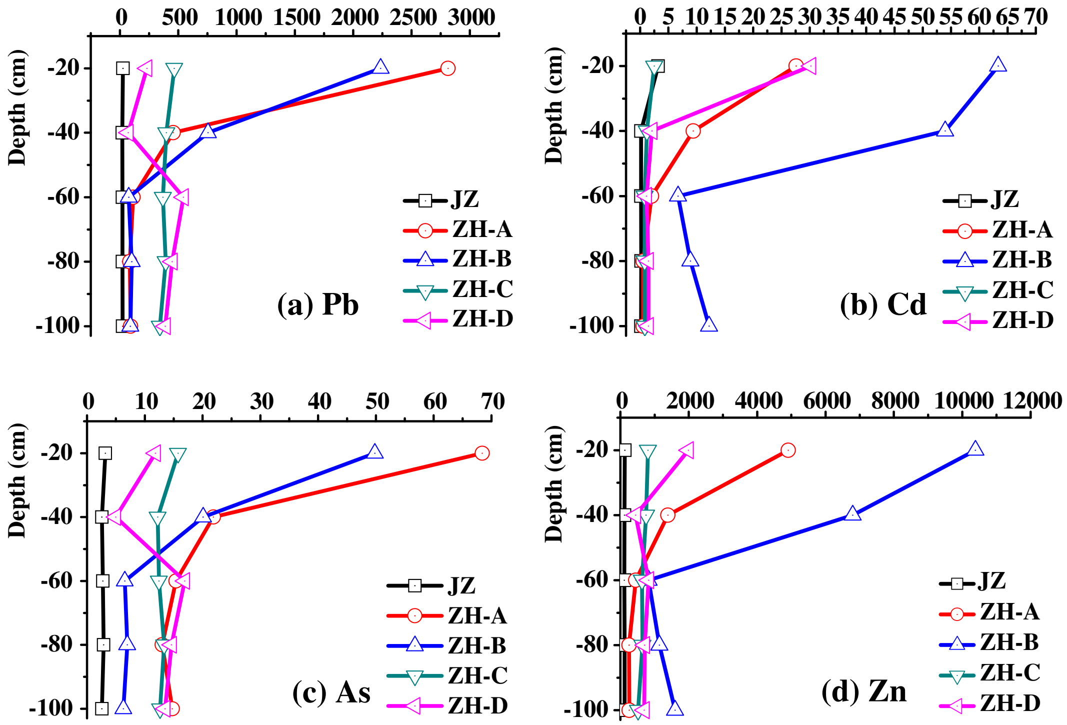

**Fig. 4** Evolution of heavy metals concentrations in soil profiles (<2 mm) (*Created by Origin 8 program*)

the Ca had an ionic radius similar to Cd (Han and Banin 1995; Rosen and Chen 2014; Li et al. 2015). As a result, Cd could easily substitute for Ca in calcium carbonate in soils, leading to a high concentration of Cd in carbonate-bond fraction. Zn ionic radius is 26 % smaller than that of Ca but can also substitute for Ca ionic in cationic sites in calcite (Reeder 1983). Previous studies in the mining area soils showed that Pb was preferably associated with the non-residual fraction (Monterroso et al. 2014; Li et al. 2015). Therefore, Cd, Zn, and Pb can reach deeper depth than As. In summary, the mobility of metals in soil profiles could be classed as Cd > Zn ≫ Pb > As. Similar phenomena were also observed by other researchers when they studied the mobility of heavy metals in a Pb-Zn smelting area (Li et al. 2015; Bi et al. 2006; Lei et al. 2010).

## Risk assessment

HQs and HIs of these villages were calculated by using the 95 % UCL measured heavy metals and As soil concentrations and U.S. EPA reference dose. The soil ingestion and skin adherence pathway for adult and child scenarios at various sampling locations were presented in Table 1. Although the soil Zn concentrations were higher at most sampling points, the hazard quotient for Pb was higher than that of Zn. For a child who lived in the AYK, the HQ for Pb through ingestion and skin adherence exposure was 16.5 (12.9 by ingestion exposure risk and 3.6 by skin adherence exposure risk), indicating that the estimated oral and skin absorption exceeded the “safe” reference dose by 15.5 times. Health risk due to oral intake and skin adherence of Pb for other villages like MSK, XC, and KS was also higher than the safe value 1, but lower than the AYK. Except for Pb, the risk to child contributed by the element arsenic through ingestion exposure also should be paid more attention. The HQ of arsenic through ingestion exposure was 4.42 in AYK and 3.90 in MSK for children, higher than the safe value 1. The risk through ingestion and skin adherence exposure to children contributed by the metals Zn and Cd was minimal (HQ ≤ 1). For the village WLP, which was the furthest point to the pollution related enterprises among all these study locations, the HI for child was lower than the safe level (=1). Among those elements, Pb contributed to the highest HQs (57.0 ~ 73.9 %) for the HI.

In comparison to children, the potential health risk of ingestion exposure for adult was lower. This was partly attributed to the higher ingestion rate used (200 mg/day

**Table 1** Estimated hazard quotients and hazard index for heavy metals and As via soil ingestion and skin adherence exposure

| | Ingestion for child | | | | Ingestion for adult | | | | Skin adherence for child | | | | Skin adherence for adult | | | | HI-child | HI-adult |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cd | Pb | Zn | As | Cd | Pb | Zn | As | Cd | Pb | Zn | As | Cd | Pb | Zn | As | | |
| **AYK** | 0.52 | 12.9 | 0.44 | 4.42 | 0.064 | 1.61 | 0.055 | 0.55 | 0.059 | 3.60 | 0.00124 | 0.37 | 0.07 | 4.58 | 0.00158 | 0.47 | 22.3 (73.9 %)[a] | 7.41 (83.5 %)[b] |
| **MSK** | 0.36 | 8.17 | 0.30 | 3.90 | 0.046 | 1.02 | 0.038 | 0.49 | 0.042 | 2.29 | 0.00085 | 0.33 | 0.05 | 2.91 | 0.00108 | 0.42 | 15.4 (67.9 %) | 4.98 (79.1 % |
| **KS** | 0.05 | 5.22 | 0.10 | 1.95 | 0.006 | 0.65 | 0.013 | 0.24 | 0.006 | 1.46 | 0.00029 | 0.16 | 0.01 | 1.86 | 0.00037 | 0.21 | 8.96 (74.7 %) | 2.99 (84.0 %) |
| **XC** | 0.12 | 1.91 | 0.08 | 0.76 | 0.015 | 0.24 | 0.010 | 0.10 | 0.014 | 0.53 | 0.00021 | 0.06 | 0.02 | 0.68 | 0.00027 | 0.08 | 3.47 (70.2 %) | 1.13 (80.8 %) |
| **GTC** | 0.04 | 0.58 | 0.03 | 0.44 | 0.005 | 0.07 | 0.004 | 0.06 | 0.004 | 0.16 | 0.00009 | 0.04 | 0.01 | 0.21 | 0.00012 | 0.05 | 1.29 (57.0 %) | 0.39 (70.2 %) |
| **LSC** | 0.05 | 0.94 | 0.04 | 0.46 | 0.006 | 0.12 | 0.004 | 0.06 | 0.005 | 0.26 | 0.00010 | 0.04 | 0.01 | 0.33 | 0.00013 | 0.05 | 1.78 (67.3 %) | 0.57 (78.6 %) |
| **WLP** | 0.04 | 0.47 | 0.03 | 0.26 | 0.005 | 0.06 | 0.003 | 0.03 | 0.005 | 0.13 | 0.00007 | 0.02 | 0.01 | 0.17 | 0.00009 | 0.03 | 0.96 (62.9 %) | 0.30 (75.1 %) |
| **JZ** | 0.01 | 0.18 | 0.01 | 0.13 | 0.001 | 0.02 | 0.002 | 0.02 | 0.001 | 0.05 | 0.00004 | 0.01 | 0.00 | 0.06 | 0.00005 | 0.01 | 0.40 (57.7 %) | 0.12 (71.1 %) |

[a] Pb contribution for the HI of child

[b] Pb contribution for the HI of adult

for child and 100 mg/day for adult) for estimating the risk and the smaller body size. The HQ of all measured metals for child and adult in the control area was at safe level (HQ < 1), and the HI was also within safe limit. Therefore, the topsoil may pose a health risk to children in AYK, MSK, KS, XC, GTC, and LSC mainly due to the high soil concentration of Pb. Namely, high soil concentration of Pb exerted great health risk to people who live there. Ivartnik and Eržen (2010) found that over 80 % of the total blood Pb load was soil related.

Figure 5 showed the HI aerial distribution of the measured metals for adult and child in the study area and control area (the HI were calculated by the concentrations of metals in the sampling point rather than 95 % UCL). The majority area of the survey region of HI for child was higher than safe value 1, especially at the points like AYK, MSK, and KS. The HI for child was higher than 10, indicating that this area was not suitable for child to live. However, we found several primary schools were in running in AYK and MSK. The HI for adult in the survey area was lower than that of the child.

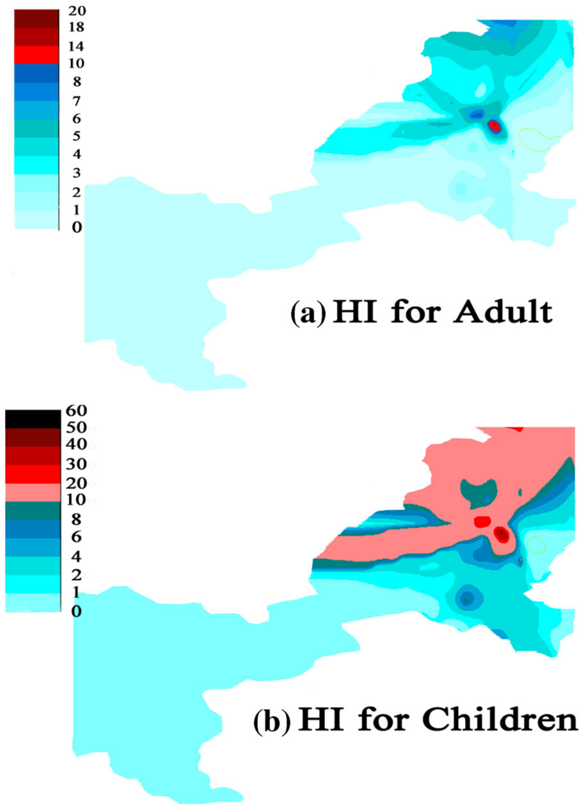

**Fig. 5** The interpolated maps of HI for adult (**a**) and children (**b**) (*created by Map-Gis 6.7 program*)

The model used in this investigation provided a useful tool for risk assessment in identifying the relative human health risks of the heavy metals in soil at different locations. However, there were inherent uncertainties including actual exposure duration and ingestion rate (Leung et al. 2008). This study only considered exposure to heavy metals and As through soil ingestion and skin adherence. In addition, risk due to consumption of food and water may also make contribution to the heavy metals absorption.

## Conclusions

The concentrations, spatial distribution, profiles, and health risk assessment of the heavy metals (Pb, Cd, Zn, and As) in Pb/Zn mining areas soils were investigated and assessed in the present study. The Cd, Pb, Zn, and As concentrations in the study area and control area showed that the smelt activities made main contribution to the high concentration of heavy metal in the topsoil. Wind direction has a great influence on the distribution of Cd, Pb, Zn, and As concentration on the topsoil of the surrounding of mining activities areas. The mobility of metals in study area soil profiles was classed as Cd > Zn ≫ Pb > As. There was a higher health risk (child higher than adult) in the study area. Lead contributed to the highest HQs for the HI since long-term Pb exposure had an irreversible effect on the development of the central nervous system and IQ (especially for child). Effective measures are needed to cure the toxic metal contamination in the study area.

**Acknowledgments** This work was financially supported by the Environmental Protection Industry Research Special Funds for Public Welfare Projects of China (Grant No. 201409022 and 201509051), the National Natural Science Foundation of China (Grant No. 41203061), and the One Hundred-Talent Plant of Chinese Academy of Sciences (CAS).

## References

Aelion, C. M., Davis, H. T., McDermott, S., & Lawson, A. B. (2008). Metal concentrations in rural topsoil in South Carolina: potential for human health impact. *Science of the Total Environment, 402*(2), 149–156.

Anju, M., & Banerjee, D. K. (2012). Multivariate statistical analysis of heavy metals in soils of a Pb–Zn mining area, India. *Environmental Monitoring and Assessment, 184*(7), 4191–4206.

Bi, X., Feng, X., Yang, Y., Qiu, G., Li, G., Li, F., et al. (2006). Environmental contamination of heavy metals from zinc smelting areas in Hezhang County, western Guizhou, China. *Environment International, 32*(7), 883–890.

Candeias, C., Melo, R., Ávila, P. F., Ferreira da Silva, E., Salgueiro, A. R., & Teixeira, J. P. (2014). Heavy metal pollution in mine–soil–plant system in S. Francisco de Assis–Panasqueira mine (Portugal). *Applied Geochemistry, 44*, 12–26.

Canfield, R. L., Henderson Jr., C. R., Cory–Slechta, D. A., Cox, C., A., J. T., & P., L. B. (2003). Intellectual impairment in children with blood lead concentrations below 10 μg per deciliter. *New England Journal of Medicine, 348*(16), 1517–1526.

Ebbinghaus, E., Kreeb, K., & Weinmann–Kreeb, R. (1997). GIS supported monitoring long–termed urban trace element loads with bark of *Aesculus hippocastanum* L. *Journal of Applied Botany, 71*(5–6), 205–211.

Gilbert, R. O. (1987). *Statistical methods for environmental pollution monitoring* (pp. 177–185). New York: John Wiley& Sons, Inc..

Gu, Y. G., Li, Q. S., Fang, J. H., He, B. Y., Fu, H. B., & Tong, Z. J. (2014). Identification of heavy metal sources in the reclaimed farmland soils of the pearl river estuary in China using a multivariate geostatistical approach. *Ecotoxicology and Environmental Safety, 105*, 7–12.

Ha, H., Olson, J. R., Bian, L., & Rogerson, P. A. (2014). Analysis of heavy metal sources in soil using Kriging interpolation on principal components. *Environmental Science & Technology, 48*(4), 4999–5007.

Han, F., & Banin, A. (1995). Selective sequential dissolution techniques for trace metals in arid-zone soils: the carbonate dissolution step. *Communications in Soil Science and Plant Analysis, 26*(3–4), 553–576.

Han, R. S., Liu, C. Q., Huang, Z. L., Chen, J., Ma, D. Y., Lei, L., et al. (2007). Geological features and origin of the Huize carbonatehosted Zn–Pb–(Ag) district, Yunnan, South China. *Ore Geology Reviews, 31*(1), 360–383.

Huamain, C., Chunrong, Z., Cong, T., & Yongguan, Z. (1999). Heavy metal pollution in soils in China: status and countermeasures. *Ambio, 28*(2), 130–134.

Hughes, M. F. (2002). Arsenic toxicity and potential mechanisms of action. *Toxicology Letters, 133*(1), 1–16.

Ivartnik, M., & Eržen, I. (2010). The IEUBK model for lead blood burden prediction in children used in the exploration and remediation of the upper Meža valley environment. *Slovenian Journal of Public Health, 49*(2), 76–85.

Jung, M. C., & Thornton, I. (1996). Heavy metal contamination of soils and plants in the vicinity of a leadzinc mine, Korea. *Applied Geochemistry, 11*(1), 53–59.

Kaufmann, R. B., Staes, C. J., & Matte, T. D. (2003). Deaths related to lead poisoning in the United States, 1979–1998. *Environmental Research, 91*(2), 78–84.

Krysiak, A., & Karczewska, A. (2007). Arsenic extractability in soils in the areas of former arsenic mining and smelting, SW Poland. *Science of the Total Environment, 379*(2), 190–200.

Lee, M. M., Wu-Williams, A., Whittemore, A. S., Zheng, S., Gallagher, R., Teh, C. Z., et al. (1994). Comparison of dietary habits, physical activity and body size among Chinese in North America and China. *International Journal of Epidemiology, 23*(5), 984–990.

Lei, M., Zhang, Y., Khan, S., Qin, P.-F., & Liao, B.-H. (2010). Pollution, fractionation, and mobility of Pb, Cd, Cu, and Zn in garden and paddy soils from a Pb/Zn mining area. *Environmental Monitoring and Assessment, 168*(1), 215–222.

Leung, A. O., Duzgoren Aydin, N. S., Cheung, K., & Wong, M. H. (2008). Heavy metals concentrations of surface dust from ewaste recycling and its human health implications in Southeast China. *Environmental Science & Technology, 42*(7), 2674–2680.

Li, H., Li, D., Xiao, T., He, L., Ning, Z., Sun, J., et al. (2008). Geochemistry and environmental effect of cadmium in the superlarge Jinding PbZn deposit, Yunnan Province, China. *Chinese Journal of Geochemistry, 27*(1), 21–27.

Li, Z., Feng, X., Li, G., Bi, X., Sun, G., Zhu, J., et al. (2011). Mercury and other metal and metalloid soil contamination near a Pb/Zn smelter in East Hunan province, China. *Applied Geochemistry, 26*(2), 160–166.

Li, W., Xu, B., Song, Q., Liu, X., Xu, J., & Brookes, P. C. (2014a). The identification of 'hotspots' of heavy metal pollution in soil–rice systems at a regional scale in eastern China. *Science of the Total Environment, 472*, 407–420.

Li, Z., Ma, Z., Van der Kuijp, T. J., Yuan, Z., & Huang, L. (2014b). A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. *Science of the Total Environment, 468*, 843–853.

Li, P., Lin, C., Cheng, H., Duan, X., & Lei, K. (2015). Contamination and health risks of soil heavy metals around a lead/zinc smelter in southwestern China. *Ecotoxicology and Environmental Safety, 113*, 391–399.

Liu, H., Probst, A., & Liao, B. (2005). Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). *Science of the Total Environment, 339*(13), 153–166.

Liu, G., Xue, W., Tao, L., Liu, X., Hou, J., Wilton, M., et al. (2014). Vertical distribution and mobility of heavy metals in agricultural soils along Jishui River affected by Mining in Jiangxi Province, China. *CLEAN–Soil, Air, Water, 42*(10), 1450–1456.

Monterroso, C., Rodríguez, F., Chaves, R., Diez, J., Becerra Castro, C., Kidd, P., et al. (2014). Heavy metal distribution in minesoils and plants growing in a Pb/Znmining area in NW Spain. *Applied Geochemistry, 44*, 3–11.

Navarro, M., Pérez Sirvent, C., Martínez Sánchez, M., Vidal, J., Tovar, P., & Bech, J. (2008). Abandoned mine sites as a source of contamination by heavy metals: a case study in a semiarid zone. *Journal of Geochemical Exploration, 96*(2), 183–193.

Ordóñez, A., Loredo, J., De Miguel, E., & Charlesworth, S. (2003). Distribution of heavy metals in the street dusts and soils of an Industrial City in northern Spain. *Archives of Environmental Contamination and Toxicology, 44*(2), 160–170.

Oves, M., Khan, M. S., Zaidi, A., & Ahmad, E. (2012). Soil contamination, nutritive value, and human health risk assessment of heavy metals: an overview. *Toxicity of Heavy Metalsl to Legumes and Bioremediation*. 1–27, Springer.

Pruvot, C., Douay, F., Hervé, F., & Waterlot, C. (2006). Heavy metals in soil, crops and grass as a source of human exposure in the former mining areas (6 pp). *Journal of Soils and Sediments, 6*(4), 215–220.

Qu, C., Sun, K., Wang, S., Huang, L., & Bi, J. (2012). Monte carlo simulationbased health risk assessment of heavy metal soil pollution: a case study in the Qixia mining area, China. *Human and Ecological Risk Assessment: An International Journal, 18*(4), 733–750.

Reeder, R. J. (1983). *Carbonates: Mineralogy and Chemistry.* Blacksburg: Mineralogical Society of America.

Rodríguez, L., Ruiz, E., Alonso Azcárate, J., & Rincón, J. (2009). Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain. *Journal of Environmental Management, 90*(2), 1106–1116.

Rosen, V., & Chen, Y. (2014). The influence of compost addition on heavy metal distribution between operationally defined geochemical fractions and on metal accumulation in plant. *Journal of Soils and Sediments, 14*(4), 713–720.

U.S. EPA. (2002). Soil screening levels for superfund sites. In soil screening levels for superfund sites. http://www.epa.gov/reg3hwmd/risk/human/rbconcentration_table/documents/SSG_nonrad_supplemental.pdf

U.S. EPA. (2012). Regional Screening Level (RSL) summary table. http://www.epa.gov/region9/superfund/prg/. Accessed 10 Jun 2014.

Zhang, C. (2006). Using multivariate analyses and GIS to identify pollutants and their spatial patterns in urban soils in Galway, Ireland. *Environmental Pollution, 142*(3), 501–511.

Zhang, X., Yang, L., Li, Y., Li, H., Wang, W., & Ye, B. (2012). Impacts of lead/zinc mining and smelting on the environment and human health in China. *Environmental Monitoring and Assessment, 184*(4), 2261–2273.

Zhao, H., Xia, B., Fan, C., Zhao, P., & Shen, S. (2012). Human health risk from soil heavy metal contamination under different land uses near Dabaoshan mine, southern China. *Science of the Total Environment, 417*, 45–54.

Zheng, N., Liu, J., Wang, Q., & Liang, Z. (2010). Health risk assessment of heavy metal exposure to street dust in the zinc smelting district, northeast of China. *Science of the Total Environment, 408*(4), 726–733.

Zhou, J. M., Dang, Z., Cai, M. F., & Liu, C. Q. (2007). Soil heavy metal pollution around the Dabaoshan mine, Guangdong Province, China. *Pedosphere, 17*(5), 588–594.

Zhuang, P., McBride, M. B., Xia, H., Li, N., & Li, Z. (2009). Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. *Science of the Total Environment, 407*(5), 1551–1561.

Żukowska, J., & Biziuk, M. (2008). Methodological evaluation of method for dietary heavy metal intake. *Journal of Food Science, 73*(2), 21–29.