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Heavy metal contamination and health risk assessment for children near a large Cu-smelter in central China

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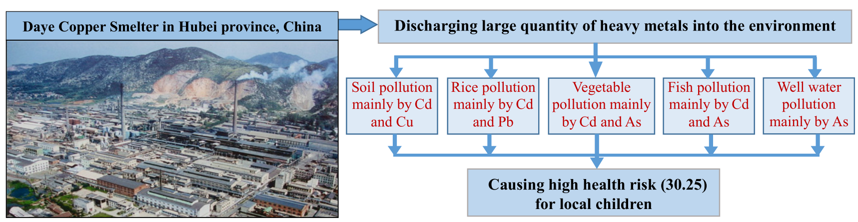
HIGHLIGHTS

- A comprehensive heavy metal pollution and health risk assessment of soil, crop, well water and fish was conducted.
- Elevated concentrations of heavy metals were found in the soil, crop, well water and fish.
- Health risk of heavy metal pollution was high for local children.
- Consumption of crops was the major contribution to risk.
- Most of the risks were due to Cd, As and Pb pollution.

GRAPHICAL ABSTRACT



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ABSTRACT

Nonferrous metallurgy is causing significant concerns due to its emissions of heavy metals into environment, degrading environmental quality, and consequently posing high risks to human health. In this study, the concentration levels of Cadmium (Cd), Copper (Cu), Lead (Pb), and Arsenic (As) were investigated in soil, crop, well water, and fish samples collected around the Daye Copper Smelter in Hubei province, China, and the potential health risks were assessed for local children. The results showed that soils near the smelter were heavily polluted by Cd, Cu, Pb, and As, with the mean concentrations of 4.87, 195.26, 92.65, and 35.84 mg/kg, respectively, which were significantly higher than the values of soil Cd (0.18 mg/kg), Cu (32.84 mg/kg), Pb (28.46 mg/kg), and As (13.65 mg/kg) in the reference area ($p < 0.001$). The concentrations of Cd and As in vegetable samples collected from smelter-affected area exceeded the maximum permissible level (MPL) for food in China by 82% and 39%, respectively. The concentrations of Cd and Pb in rice grain harvested from smelter-affected area were 9.35 and 1.35 times higher than the corresponding MPL, respectively. The concentrations of Cd, As, and Cu in fish muscle from smelter-affected area exceeded the national MPL by 72%, 41%, and 24% of analyzed samples, respectively. The concentrations of Cd ($p < 0.05$) and As ($p < 0.01$) in well water were significantly higher in the smelter-affected area than those in the reference area, respectively. The health risks to local children in the smelter-affected area were 30.25 times higher than the acceptable level of 1, and most of the risks were resulted from Cd (46%), As (27%) and Pb (20%). The intake of crops was a major source (78%) to health risks for local children.

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1. Introduction

Heavy metal (HM) pollution caused severe environmental and health-related problems around the world (Spurgeon et al., 2011). They are particularly hazardous due to their persistence and toxicity, and adverse effects to the environment and human health (Cao et al., 2014). In China, about 20 million ha of farmland and 12 million tons of grains were contaminated by HMs every year (G. Li et al., 2011; Z.G. Li et al., 2011). A large portion of this pollution came from metal smelting (Li et al., 2014). HMs emitted from those smelters are transferred to different environmental media, such as air, soil, crop, dust and water, can eventually enter the human bodies through direct ingestion or food chains, and pose potential threats to human health (Carrizales et al., 2006; Spurgeon et al., 2011). Generally, Cd, As and Pb are considered as potential carcinogens and are associated with etiology of many diseases, especially cardiovascular, liver, kidney, bladder, nervous system, blood and bone diseases (Cai et al., 2015). Although Cu is an essential trace element, its excessive concentration can threaten human health (Zhou et al., 2018). Recent studies also showed that Cu toxicity could induce changes in cellular activities, such as regulation of lipid metabolism, neuronal activity, gene expression and resistance of tumor cells to chemotherapeutic drugs (Gaetke et al., 2014). Elevated contents of HM in air, soil, dust, water and plant in smelter-affected areas have been frequently reported in many countries, including France (Douay et al., 2013), England (Spurgeon et al., 2011), Australia (Mackay et al., 2013), and China (Li et al., 2014). Many previous studies reported high contents of HMs in the urine and blood samples of local residents, particularly children living near metal smelters (Cui et al., 2005; Spurgeon et al., 2011).

Metal smelting was considered as one of the most important anthropogenic sources of HM emission (Zheng et al., 2007). Cu, Pb, As and Cd had similar geochemical characteristics, and co-existing in Cu ore together. During Cu smelting process, HMs in Cu ores would be emitted into the surrounding environment via waste gas, waste water, and waste residue. Therefore, their pollution to the surrounding environment from those metal smelters had been widely studied (Douay et al., 2013; Mackay et al., 2013). Smelting activities of the Daye Copper Smelter (DCS), which have been operating for >60 years, discharged a large amount of smelt waste into the surrounding environment without any proper treatment. Previous studies found that soil (Du et al., 2015), river water (Wang and Wang, 2007), and sediment (Zhang et al., 2014) near the smelter were heavily contaminated by HMs. On the other hand, few studies systematically delineated the pollution scope of different environmental media, the extent of human exposure via multi-pathways, and the potential health consequences in the studied area and other areas near large copper smelters around the world (Zhou et al., 2018). Children are especially sensitive to HMs poisoning because of the child-specific physiological and behavior patterns (Cao et al., 2015). Health-related incidents for children such as Cd, As and Pb poisoning have attracted widespread attention (Cao et al., 2014), particularly around smelter-affected areas (Carrizales et al., 2006; Spurgeon et al., 2011). Therefore, assessing health risks for exposure to various HMs through different environmental media and the main pathways in smelter-affected area would be very important for protecting children's health. The aims of the study were: (1) quantify the content levels of HMs in multiple environmental media (i.e., soil, crop, well water, and freshwater fish) near DCS, and (2) assess the daily intakes and health risks of HMs to local children.

2. Materials and methods

2.1. Studied area

Daye city (114°31′–115°20′, 29°40′–30°15′N) is situated at the southeast in Hubei province, central China. The climate represents a temperate monsoonal continent with average annual rainfall of 1385.9 mm and average temperature of 16.9 °C. The primary wind direction is from southeast to northwest. As one of the largest Cu-smelter in China, the DCS located at the north of Daye city (Fig. 1). It was built in 1953 and produces about 250,000 t Cu every year (Wang and Wang, 2007). During Cu smelting process, Cd, Pb, As and Cu are emitted into the surrounding environment in great quantities via atmospheric deposition, sludge applications, and wastewater irrigation. The discharge loadings of Cd and Pb are approximately 0.5 t and 2 t by wastewater annually, respectively (Zhang et al., 2014). According to our field survey, these areas near the north of the DCS are mountains, and villages mainly concentrated in the southwest of the DCS. In addition, some villages had been discarded because of serious pollution from the DCS. Therefore, remaining ten villages (V1, V2, V3, V4, V5, V6, V7, V8, V9, and V10) near the DCS were as the exposed area, and one village (Liurenba) which was not polluted by the DCS as the reference area (Fig. 1). According to our survey, V8, V9, and V10 were mainly affected by atmospheric deposition from the smelter since they were under the direction of the dominant wind, and other villages were mainly contaminated by wastewater irrigation and atmospheric deposition from the smelter.

2.2. Sample collection and analysis

2.2.1. Questionnaire survey

A questionnaire survey was conducted in the study area to obtain key risk factors, such as the dietary behavior and the weight of the local children. The information extracted from the questionnaire included the intake rate of each crop, fish and drinking water per day per child. In total, 65 children who were native-born and aged from 3 to 7 years old participated in the questionnaire survey. The average daily intake rate of each crop and fish over a whole year was calculated (Chen et al., 2018).

2.2.2. Field sampling

Soil samples (1 kg) were obtained from the upper horizon (0–20 cm in depth) at 136 sites, including 102 from the exposed area and 34 from the reference area. At each site, soils were randomly sampled at 3–5 locations and bulked together to form a composite sample (Cai et al., 2015). In the study area, the drinking water was well water. A total of 24 well water samples (20 from the exposed area, and 4 from the reference area) were collected with 1 L acid-washed polyethylene bottles from local families. During sampling, two drops of ultrapure nitric acid were added into water samples, then refrigerated and stored at −20 °C (Cao et al., 2014).

Standing food crop samples including maize, rice, carrot, ipomoea, radish, lettuce, red cabbage, cabbage, pakchoi and celery were also obtained. 18 maize grain, 22 rice grain, 13 carrot, 15 ipomaea, 13 radish, 13 lettuce, 13 red cabbage, 14 cabbage, 15 pakchoi, and 12 celery samples were collected (1 kg) directly from the land with paired soil samples. At each site, 3–5 sub-samples were collected and mixed to form one representative sample (Ji et al., 2013). Additionally, 44 freshwater fish samples including 10 Wuchang carp, 14 grass carp, 11 crucian carp, and 9 bighead carp were obtained from ponds and rivers, because they were consumed relatively in high amounts in the area. All fish samples were washed thoroughly with fresh water for the sake of removing mud and other fouling substances, and were stored in clean polyethylene bags with ice immediately and frozen at −20 °C (Zhong et al., 2018). The types and numbers of samples in every village were shown in Table S1.

2.2.3. Sample treatment and analysis

The water samples were filtered with 0.45 μm filter paper and stored at 0–4 °C before element analysis (Cai et al., 2015). After being air-dried at room temperature for two weeks (ISO-11464, 2006), ground, and sieved with a 1 mm stainless-steel mesh, soil samples (0.1 g each) were prepared with acid digestion (Cao et al., 2015). After washed

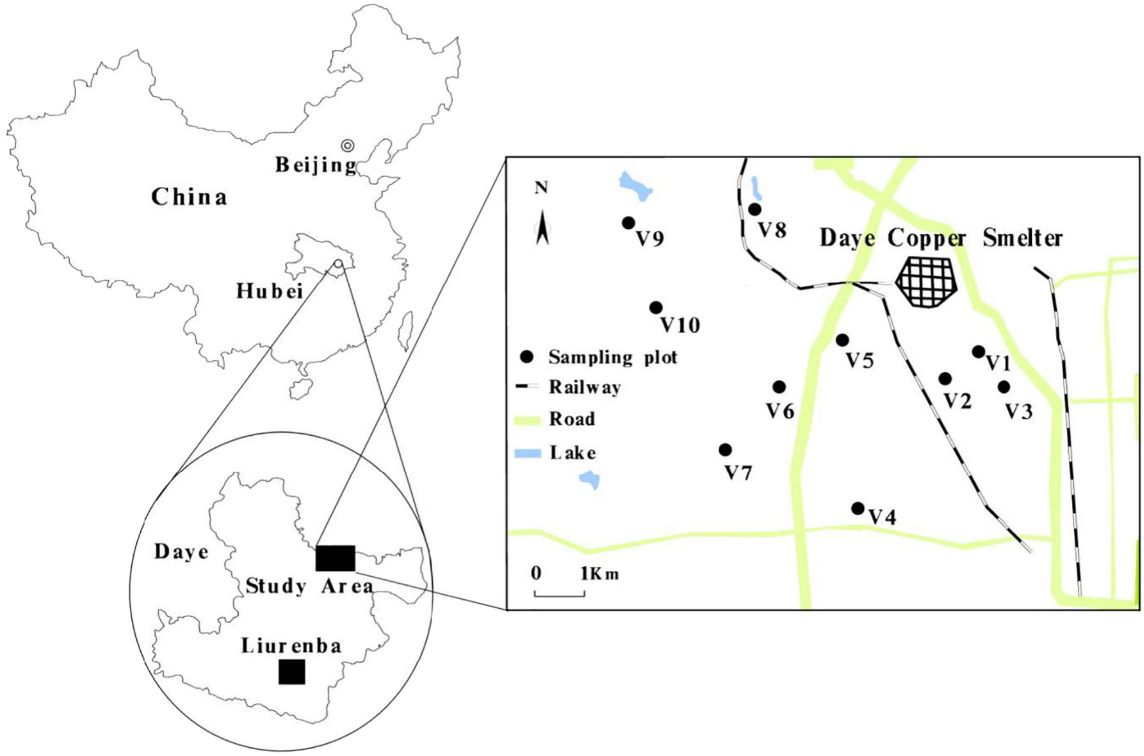

Fig. 1. Locations of sampling villages.

using tap water and deionized water thoroughly, the edible parts of crop samples were cut into small pieces. After these small pieces were dried at 60 °C, they (0.5 g each) were ground and sieved. After being thawed at room temperature, fish samples were dissected using cleaned knife to obtain muscle tissues. Subsequently, these muscle samples were washed thoroughly with Milli-Q water. Finally, 20 g muscle tissues were oven dried at 60 °C, and then these samples were powdered in glass mortar, sieved with 1 mm mesh, and transferred to porcelain dishes (Zhuang et al., 2013).

Soil organic matter (SOM) was measured with the Walkley-Black's procedure reported by Nelson and Sommers (1982), and soil pH levels were determined in 2.5:1 water/soil suspension. The contents of HMs were tested as described by Cai et al. (2015). Briefly, Soil, plant, and fish samples were digested with concentrated acid mixtures of $HClO_4$, HNO_3 and HF, $HClO_4$ and HNO_3, and HNO_3 and H_2O_2, respectively. All digested solutions were filtered and diluted with distilled water to appropriate contents for instrumental analysis. The contents of HMs in all samples were analyzed using an ICP-MS (Agilent-7500c, Agilent Scientific Technology Ltd., USA) under optimized conditions (Cao et al., 2015). A solution containing rhenium and rhodium was added online using a Y-type canal as an internal standard and subjected to concentration measurements. The results were quantified with an empirical calibration curve obtained from the analysis of a multi-element calibrations standard material (Agilent Scientific Technology Ltd., USA).

To control quality, each digestion batch included a reagent blank, a representative reference standard, an analytical blank and duplicate, comprised of 10% of the total samples, respectively, to assess the accuracy and precision of the analysis (Cao et al., 2014). Standard reference materials obtained from the National Research Centre for Certified Reference Materials, China, including GBW07403 (soil), GBW08573 (fish), and GBW07602 (plant), were used for validation of the analytical procedure. Replicate analysis of these reference materials showed good accuracy, with recovery rates of the elements were 88%–113%. All chemical reagents were guaranteed reagents in the experiments. All glass tubes and bottles were previously soaked overnight in HNO_3 (20%) and rinsed thoroughly with distilled water before use. The limit of detection (LOD) and limit of quantification (LOQ) were defined as 3 and 10 times the standard deviation of 11 runs of blank measurements, respectively. The LODs for Cd, Cu, Pb and As were determined as 0.03, 0.02, 0.2 and 0.03 μg/L, respectively, and the LOQs for Cd, Cu, Pb and As were 0.1, 0.05, 0.5 and 0.1 μg/L, respectively.

2.3. Data analysis

2.3.1. Pollution load index

The pollution load index (PLI) was used to characterize the degree of soil contamination for each metal. It was a ratio of metal contents in the exposed soils to those in reference soils (Cai et al., 2015):

$$\mathrm{PLI} = \frac{\mathrm{Csoil\ \ (exposed)}}{\mathrm{Csoil\ \ (Reference)}} \tag{1}$$

where C_{soil} (exposed) and C_{soil} (Reference) were the contents of HMs in the exposed and reference soils, respectively.

2.3.2. Exposure assessment of heavy metals

According to the Exposure Factors Handbook (US EPA, 1997), the average daily intake of metals (DIM) for children through soils, drinking water and foods can be calculated with the following equation:

$$\mathrm{DIM} = \sum_{i=1}^{n} \frac{\mathrm{Ci} \times \mathrm{IRi} \times \mathrm{EFi} \times \mathrm{EDi}}{\mathrm{BW} \times \mathrm{ATi}} \tag{2}$$

where C_i represents the content of HMs in the environmental media i (mg/kg or μg/L); IR_i is the daily ingestion rate to the exposure medium i (mg/day or L/day); EF_i is the exposure frequency (365 days/year); ED_i is the exposure duration (7 years for children were assumed in this study, equivalent to the average lifetimes (Chen et al., 2018)). BW refers to the average body weight and AT_i is the average exposure time for non-carcinogenic effects (ED × 365 days/year). The average daily IR of the soil is set to 0.1 g/day in the study (US EPA, 1997). According to our questionnaire survey, the average daily IR for rice, maize, vegetable, fish and drinking water for local children were 125 g/day, 12 g/day, 94 g/day, 28 g/day and 1.1 L/day, respectively, and the BW of local children was 18.7 kg in the study area.

2.3.3. Calculation of health risk

The health risks for local children were assessed based on the hazard quotient (HQ). The HQ is a ratio of the DIM to the specific reference dose (RfD) for each metal, as follows:

$$\mathrm{HQ} = \frac{\mathrm{DIM}}{\mathrm{RfD}} \tag{3}$$

where RfD is the maximum allowable risk for humans due to daily exposure. If the HQ value <1, there are not obvious health risks. However, if the HQ value ≥1, there are potential risks, and protective measures should be taken (Cao et al., 2015). The RfDs were based on 1, 0.5, 40 and 0.3 μg/kg/d for Cd-food, Cd-water, Cu and As, respectively (US EPA, 2018). The U.S. Environmental Protection Agency had not established the RfD for Pb (US EPA, 2018). With new available data that the value of provisional tolerable weekly intake (PTWI) of 25 μg/kg bw for Pb could be responsible for a drop of 3 points in the IQ in children and an increase in systolic blood pressure in adults, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) acknowledged that established PTWI value was not sufficiently protective but that they were unable to establish a new health-based guidance value (JECFA, 2011; Jovic and Stankovic, 2014). The European Food Safety Authority concluded that Pb had the most harmful effect on the central nervous system of young children and on the cardiovascular system of adults, and identified three reference dietary intake values, 0.63 μg/kg bw/d for nephrotoxic effects in adults, 1.50 μg/kg bw/d for cardiovascular effects in adults and 0.50 μg/kg bw/d for neuro-developmental effects in children (EFSA, 2010; Yap et al., 2016). So the RfD for Pb used in this study was 0.50 μg/kg bw/d for children.

In addition, to assess the cumulative risks posed by various HMs (e.g., i), the HQ values of all HMs were summed and expressed as an integrated Hazard Index (HI) (US EPA, 1986):

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{HQi} \tag{4}$$

Since HMs could enter into human through different exposure pathways (EPs), total hazard index (HIt) was used to reflect health risks through different EPs and expressed as in the following equation (US EPA, 1989):

$$\mathrm{HIt} = \sum_{i=1}^{n} \mathrm{HI}\,(\mathrm{EPi}) \tag{5}$$

Chronic health risks are assumed to be non-existent if HIt <1. In contrast, risks are likely to occur if HIt ≥1, then further analysis separating the HIt would be preferable (Cao et al., 2014).

2.4. Statistical analysis

Standard statistical analyses (mean, standard deviation, coefficient of variation, skewness, kurtosis, etc.) were carried out to describe soil properties and HM concentrations. The Kolmogorov–Smirnov (K–S) test was used to determine whether the HM concentrations were normally distributed (Tian et al., 2017). A variance analysis of HM contents ($p < 0.05$) between the exposed area and reference area was employed by using a one-way ANOVA test (Tukey HSD). Independent sample *t*-tests were performed to examine the significance of the differences in the mean contents of HMs between the exposed area and reference area. The level of significance was set at $p < 0.05$ (two tailed). Correlation analysis, principal component analysis (PCA), and cluster analysis (CA) are the most common multivariate statistical methods used to identify the relationship among HMs in environmental studies and their possible sources (Cai et al., 2012). PCA was performed with varimax rotation with Kaiser normalization because orthogonal rotation minimizes the number of variables with high loading on each component and facilitates the interpretation of results, and the HM concentration data (the variables) were standardized by means of z-scores before CA and Euclidean distances for similarities in the variables were calculated in the study. Non-detects (NDs) were included in the calculations as a proxy value of a limit of detection/square root of 2 (Ji et al., 2013). The data were statistically analyzed using the statistical package SPSS 22.

3. Results

3.1. Heavy metals in soils

The HM contents and physicochemical properties in the exposed and reference soils are presented in Table 1. The K–S test confirmed that pH and SOM in both the exposed and reference soils were normally distributed ($p > 0.05$). As shown in Table 1, both the exposed and reference soils were weakly acidic with the average pH of 6.28 and 6.48, respectively. The results suggested that smelting activity decreased soil pH by 0.2 units as compared the exposed soils to the reference soils. The SOM was not significantly different, which was 6.58–28.85 mg/kg in the exposed area, and 11.58–23.62 mg/kg in the reference area. The contents of soil Cd, Cu, Pb and As in the reference area varied between 0.05 and 0.59, 15.68 and 74.36, 11.65 and 48.69, and 8.63 and 33.62 mg/kg, with average concentrations of 0.18, 32.84, 28.46 and 13.65 mg/kg, respectively. However, the concentrations of soil Cd, Cu, Pb and As in the exposed area varied between 0.08 and 29.58, 32.50 and 615.45, 42.65 and 274.86, and 12.24 and 95.68 mg/kg, with average concentrations of 4.87, 195.26, 92.65 and 35.84 mg/kg, respectively, were significantly higher than those of the reference soils ($p < 0.001$) (Table 1).

Pearson correlation analysis, PCA and CA were used to obtain the possible sources of soil HMs in the exposed area. Table S2 presents the correlation coefficients between soil properties and HMs in the exposed soils. The significantly positive correlations were found between pH and Cu ($r = 0.35, p < 0.001$), pH and Pb ($r = 0.37, p < 0.001$), pH and Cd ($r = 0.21, p < 0.05$), pH and As ($r = 0.22, p < 0.05$), and SOM and Cu ($r = 0.23, p < 0.05$). The high correlations between HMs may reflect that these HMs had similar sources (Micó et al., 2006). A significantly positive correlation at $p < 0.001$ was found between the elemental pairs Cd–Pb (0.48), Cd–As (0.83), Cu–Pb (0.94), Cu–As (0.66), and Pb–As (0.78), this indicates possible same sources for these elements.

The results of PCA by applying varimax rotation with Kaiser normalization for total metal concentrations in the exposed soils are shown in Table S3. The eigenvalue of the first extracted factor was greater than one, and the second became greater than one after the matrix rotation. The results indicated that PCA leads to a reduction of the initial dimension of the dataset to two components which explain 96.59% of the data variation (Table S3). The first principal component (PC1) explains 65.36% of the total variance and loads heavily on Cd, Cu, Pb, partially, As. The second principal component (PC2), dominated by As, partially, Cd, accounts for 31.23% of the total variance. The CA results for HMs in the exposed soils are shown in Fig. S1 as a dendrogram. The figure displays two clusters: (1) Cu–Cd–Pb; (2) As. Thus, CA results suggested at least two different sources of HMs in the exposed soils, in total agreement with the PCA results.

3.2. Heavy metals in crops

The contents (dry weight) of HMs in the edible part of crops harvested from the exposed area are presented in Fig. 2. The contents of Cd were 0.25–3.77 mg/kg (Fig. 2a) in the crops from the exposed area, and were significantly higher than those harvested from the reference

Table 1
Characteristics of the exposed and reference soils in the study area.

Properties	Exposed soils (n = 102)						Reference soils (n = 34)						Values of F
	Range	Mean (SD)	CV	Skewness	Kurtosis	K–S_P	Range	Mean (SD)	CV	Skewness	Kurtosis	K–S_P	
pH (water)	4.18–7.86	6.28 (0.96)	0.15	−0.54	−0.65	1.285	5.28–7.52	6.48 (4.32)	0.67	0.84	0.92	0.138	1.53
SOM (g/kg)	6.58–28.85	15.68 (8.75)	0.56	0.87	1.12	0.184	11.58–23.62	15.52 (9.65)	0.62	0.95	0.58	0.255	0.95
Cd (mg/kg)	0.08–29.58	4.87 (6.43)	1.32	3.20	7.62	0.000	0.05–0.59	0.18 (0.15)	0.83	1.26	1.18	0.035	18.17***
Cu (mg/kg)	32.50–615.45	195.26 (142.48)	0.73	2.16	3.15	0.000	15.68–74.36	32.84 (28.63)	0.87	0.81	0.93	0.096	42.38***
Pb (mg/kg)	42.65–274.86	92.65 (43.52)	0.47	1.92	3.05	0.000	11.65–48.69	28.46 (15.68)	0.55	0.54	0.87	0.843	68.58***
As (mg/kg)	12.24–95.68	35.84 (23.34)	0.65	1.36	0.81	0.000	8.63–33.62	13.65 (8.35)	0.61	0.68	0.73	0.796	28.72***

SD: standard deviation. CV: coefficient of variation. K–S_P is the significance level of Kolmogorov–Smirnov test for normality.
*** $p < 0.001$.

area ($p < 0.001$). As shown in Fig. 2b, the contents of Cu in the samples of radish, carrot, red cabbage and pakchoi were significantly higher than those harvested from the reference area ($p < 0.001$). The contents of Pb (Fig. 2c) and As (Fig. 2d) in the crops from the exposed area were significantly higher than those from the reference area ($p < 0.01$). These results indicate that agricultural crops grown near the DCS have been heavily contaminated by HMs. Previous studies have also reported elevated contents of HMs in food crops grown near metal smelter (Douay et al., 2013; Kwon et al., 2017; Li et al., 2014).

3.3. Heavy metals in fish and well water

The HM contents in fish muscle are listed in Fig. 3. The contents of all measured elements in fish samples in the exposed area were significantly higher compared with those in the reference area ($p < 0.05$), particularly, Cd contents in the grass carp and Wuchang carp, Cu contents in the crucian carp, and As contents in the grass carp and crucian carp in the exposed area were significantly higher than those in the reference area ($p < 0.001$). The results indicate that fish in the exposed area were seriously polluted by these HMs due to smelting activities of the DCS. The contents of HMs were in the order of Cu > As > Pb > Cd in fish muscle collected from the exposed area. On average, the highest contents of Cd and Pb were in the grass carp samples, with 0.41 and 0.48 mg/kg. However, the highest contents of Cu and As were in the bighead carp and crucian carp samples, with 8.76 and 0.73 mg/kg, respectively.

The HM contents in well water are listed in Table S4. The contents of well water Cd, Cu, Pb and As in the exposed area varied between ND and 0.92, 0.50 and 6.80, ND and 1.34, and 0.37 and 33.91 μg/L, with average concentrations of 0.17, 3.25, 0.54 and 6.31 μg/L, respectively. However, the concentrations of well water Cd, Cu, Pb and As in the reference area varied between ND and 0.16, 0.08 and 12.35, ND and 0.95, and 0.12 and 6.53 μg/L, with average concentrations of 0.07, 2.52, 0.39 and 1.36 μg/L, respectively (Table S4). The contents of HMs were in the order of As > Cu > Pb > Cd in the exposed area, and Cu > As > Pb > Cd in the exposed area, respectively. The contents of As ($p < 0.01$) and Cd ($p < 0.05$) were significantly higher in the exposed area than those in

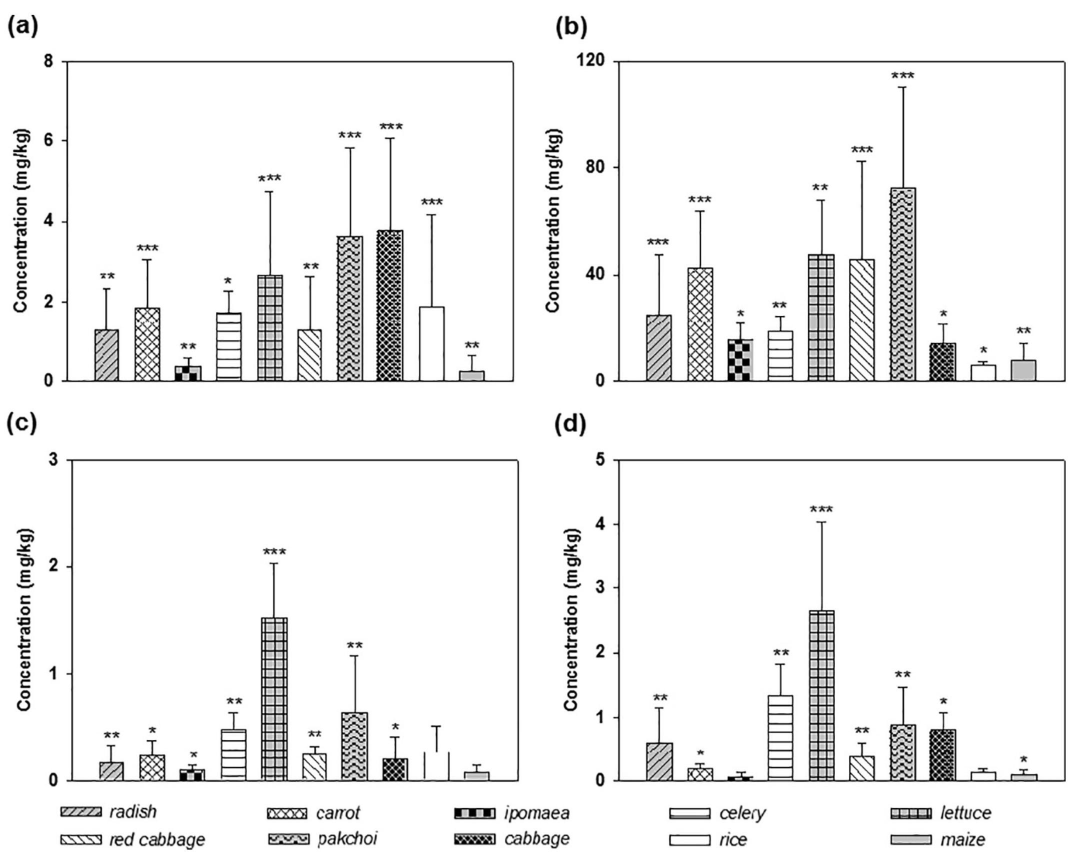

Fig. 2. The contents of heavy metals (dry weight) in the edible parts of plants collected from the exposed area: (a) Cd; (b) Cu; (c) Pb; and (d) As. The error bars indicate the standard deviation while the asterisks indicate significant differences in contents of heavy metals between plants collected from the exposed and reference areas, at $p < 0.05$ (*), $p < 0.01$ (**) and $p < 0.001$ (***), respectively.

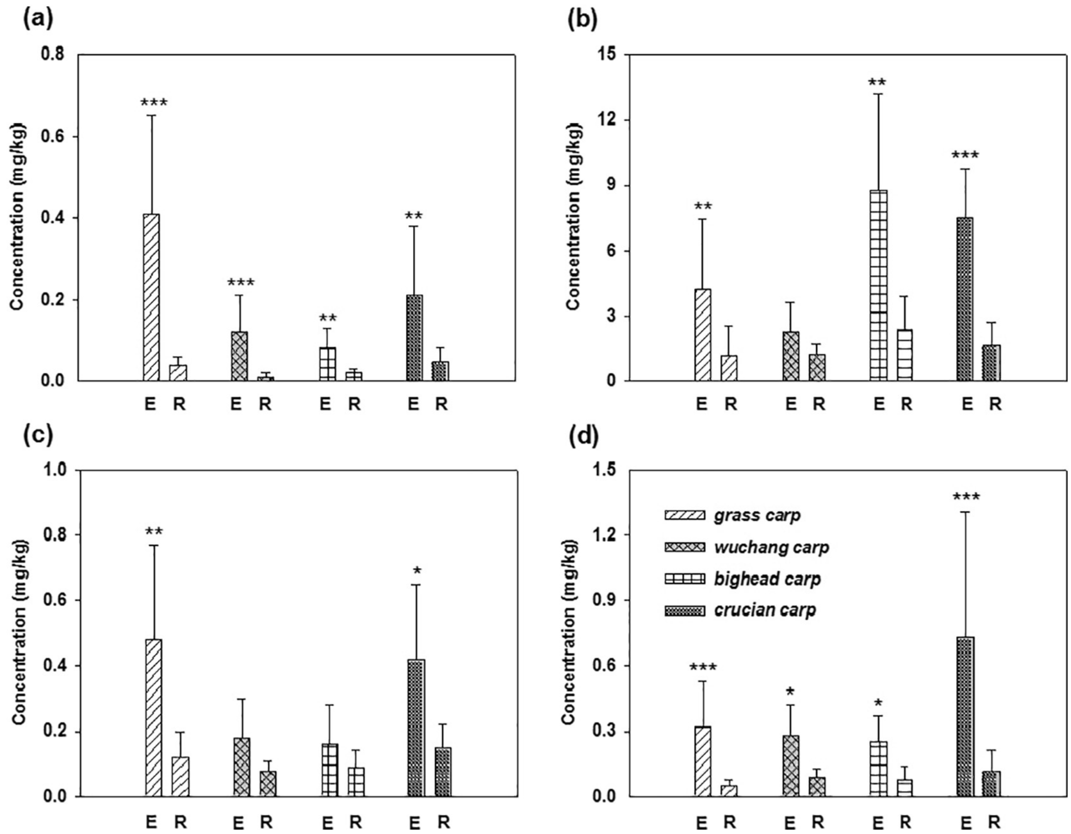

Fig. 3. The contents of heavy metal (wet weight) in the muscle of fish samples between the exposed (E) and the reference (R) areas: (a) Cd; (b) Cu; (c) Pb; and (d) As. The error bars indicate the standard deviation while the asterisks indicate significant differences in contents of heavy metals between fish samples obtained from the exposed and reference areas, at $p < 0.05$ (*), $p < 0.01$ (**) and $p < 0.001$ (***), respectively. E: exposed area, R: reference area.

the reference area. These results suggest that well water in the exposed area may have been polluted by element As and Cd due to smelting activities.

3.4. Dietary intake of metals and hazard quotients for local children

The total DIM of HMs for local children in the study area through the ingestion of soil, drinking water, crops and fish are presented in Table S5. The DIM of Cd, Cu, Pb and As were 14.00, 70.15, 3.09 and 2.49 μg/kg bw·d in the exposed area, and 0.51, 21.81, 1.30 and 0.95 μg/kg bw·d in the reference area, respectively, with intake from rice being greater than from other ingestion pathways for all metals (Fig. S2). The HQs of metals for local children are given in Table 3. The HQs of Cd, Cu, Pb and As through the ingestion of soil, drinking water, crops and fish were 14.01, 1.76, 6.17 and 8.31 in the exposed area, and 0.51, 0.53, 2.60 and 3.16 in the reference area, respectively.

4. Discussion

4.1. Sources of heavy metal contamination in soils

The proportions of samples in which the HM concentrations were in the range of worldwide uncontaminated soils (Kabata-Pendias and Pendias, 1992) were 97% for Cd, 97% Cu, 100% for Pb and 88% for As in the 34 reference soils, respectively. Moreover, compared with related background values of Hubei province (CNEMC, 1990, Table S6), the average contents of reference soil Cd, Cu, Pb and As were only slightly high by 6%, 7%, 6% and 10%, respectively, and therefore can represent regional baseline contents. The average PLIs in the exposed soils calculated based on the reference soils were 27.06 (Cd), 5.95 (Cu), 3.26 (Pb) and 2.63 (As), respectively. These results showed that smelting activity elevated the contents of soil HMs, and similar results were also reported in previous studies (Douay et al., 2013; Li et al., 2014).

The extent of soil contamination can be assessed on the basis of Grade II of the Chinese Environmental Quality Standard for Soils (SEPAC, 1995, Table S6) which should not be exceeded if the soil is used for agricultural purposes. As shown in Table 1, these exposed soils were heavily polluted by Cd, Cu and As, with the average contents being 16.23, 3.91 and 1.19 times higher than the corresponding maximum allowable concentrations (MAC), respectively. Moreover, both Cd and Cu contents in 100 soil samples in the exposed area were above the corresponding MACs, accounting for 98% of all samples compared with the corresponding value for Pb of 2 samples (2%), and As of 42 samples (41%). These results illustrate that the soils near the DCS may not be suitable for agricultural purposes.

Large coefficients of variation (CV) were found in all HMs in the exposed soils (Table 1), this indicated the wide variation of concentrations of these elements. Compared with the reference soils and the background soils of Hubei province, the extremely elevated concentrations of HMs were found in the exposed soils. High concentrations coupled with high CV values suggest anthropogenic sources for these elements (Cai et al., 2012). The PCA results indicated that Cd, Cu, Pb, partially, As had a common source, while As, partially, Cd had another common source. The correlation coefficient analysis and CA results were consistent with these interpretations. The PC1 could be defined as an anthropogenic component related to smelting activities since the DCS is the main pollution source in the exposed area, which has been operating for >60 years and discharged large quantities of smelt waste into the surrounding environment. The PC2 could be considered as an anthropogenic component related to agronomic practices. According to our investigation in the study area, Large amounts of fertilizers (685 kg/ha) and pesticides (26 kg/ha) are applied each year. Moreover, according to previous reports (Hu et al., 2018; Luo et al., 2009), inorganic As compounds such as calcium arsenate, sodium arsenate and many others were used largely as pesticides or herbicides, thus, they were important sources of As to soil. Livestock manures and fertilizers were also important sources of As entering agricultural soils (Cai et al., 2012). Cadmium is usually considered as a marker element of agronomic practices which include the use of livestock manure and chemical fertilizers etc. (Sun et al., 2013). For example, Cd was found predominantly in phosphatic fertilizers because Cd is commonly present as an impurity in phosphatic rocks (Luo et al., 2009). Moreover, livestock manures present significant Cd concentrations, thus, they may also be an important source of Cd to soil (Huo et al., 2010).

4.2. Heavy metal contamination in crops

The accumulation of HMs in the crops could have direct impacts on the health of local children, because crops produced in the area are mostly consumed locally. Therefore, the HM contamination in the crops could be a major health concern to local children (Cai et al., 2015). The contents of Cd, Cu, Pb and As in vegetable samples are 0.11–0.32, 1.19–6.13, 0.01–0.13 and 0.02–0.23 mg/kg fresh weight in the exposed area, respectively (Table 2). Based on the MHPRC (2005), the MACs for vegetables and cereals are Cd (0.05–0.2 mg/kg), Cu (10–10 mg/kg), Pb (0.2–0.2 mg/kg) and As (0.05–0.15 mg/kg), on a fresh weight basis. The vegetable samples in the exposed area with 82% (Cd), 39% (As) and 7% (Cu) exceeded the corresponding MACs, with mean contents of Cd and As being 3.79 and 1.48 times the MACs, respectively (Table 2). However, all vegetables had the acceptable Pb level in the exposed area.

Rice is the most important food in the area, and accumulated 0.03–9.33 mg/kg of Cd, 2.90–8.50 mg/kg of Cu, 0.05–0.92 mg/kg Pb, and 0.06–0.26 mg/kg of As in grain samples in the exposed area. The contents of Cd and Pb in rice grain in the exposed area exceeded the corresponding MAC for 83% and 50% of the samples, and in average 9.35 and 1.35 times higher than the MAC, respectively (Table 2). These results indicate that rice has some ability to transfer soil Cd and Pb into grain (Cai et al., 2015). It is widely accepted that Cd is one of the most toxic and mobile metals among all HMs, and can be readily absorbed by rice and transferred to grain where it can accumulate to higher levels and enter food chain, eventually pose health risks to consumers (Kwon et al., 2017). The As content in rice grain from the exposed area exceeded the corresponding MAC for 44% of the samples (Table 2), and was higher than those in rice grains from uncontaminated soils (Jung et al., 2005) and background As contents in rice grains in Guangdong province (Liang et al., 2003). Element As was absorbed by rice more effectively than other cereals, mainly because of flooded anaerobic environment in paddy soils (G. Li et al., 2011; Z.G. Li et al., 2011).

4.3. Heavy metal contamination in fish and well water

The accumulation of HMs in fish can pose potential health risks to the fish as well as to humans who consume them (Cai et al., 2015). Although fish muscle tended to accumulate low concentrations of HMs, it is important to compare them with the known safety levels because muscle constitutes the greatest consumed mass of the fish (Zhuang et al., 2013). According to the MAPRC (2006) and MHPRC (1994), the MACs for fish are Cd (0.1 mg/kg), Cu (50 mg/kg), Pb (0.5 mg/kg) and As (0.5 mg/kg) wet weight, respectively. The Cd contents (0.08–0.41 mg/kg) in all fish muscle from the exposed area with 72% exceeded the MAC. The contents of Cd in the grass carp, Wuchang carp and crucian carp from the exposed area were 4.1, 1.2 and 2.1 times higher than the MAC, respectively (Fig. 3). The results were higher than the same fish species (0.05–0.32 mg/kg) from the Tonglushan mine, China (Cai et al., 2015), and freshwater fish reported by Zhong et al. (2018). Similarly, the As contents (0.25–0.73 mg/kg) in fish samples in the exposed area with 41% were beyond the MAC, and the content of As (0.73 mg/kg) in the crucian carp were 1.46 times greater than the MAC. The content of As in fish samples in the exposed area were higher than those (0.13–0.68 mg/kg) from the Tonglushan mine, China (Cai et al., 2015), and in 4 kinds of fish reported by Jiang et al. (2014). For Pb, about 24% of the fish samples in the exposed area were above the MAC. However, the contents of Cu in all fish samples in the exposed area were below the corresponding MAC.

Compared with the MACs of drinking water standard in China (MHPRC, 2006), the contents of all measured HMs in well water samples collected from the exposed area were lower than their MACs, except As contents in four samples (10.98, 13.95, 14.31, and 33.91 μg/L) being beyond the MAC (10 μg/L). On the whole, the As content of well water in the exposed area was higher than the Tonglushan mine area, China (Cai et al., 2015), and the Pb and Cd contents were similar, but the Cu content was lower. However, the contents of As and Cd in the exposed area were higher than those in the groundwater reported by Wongsasuluk et al. (2018), but Pb content was lower. In addition, the contents of all HMs except As in the study were lower than those in groundwater of Buddeun mine areas, South Korea (Kim et al., 2017).

4.4. Health risks for local children

In general, soil, food and drinking water are the most important EP for ordinary human to HMs (Cao et al., 2015). In the study, the mean HIt for all HMs was 30.25 in the exposed area (Table 3), indicating a higher potential health risk to the local children when compared to some previous findings (Cai et al., 2015; Chen et al., 2018). The HQs of each metal in the exposed area were in the order of Cd (14.01) > As (8.31) > Pb (6.17) > Cu (1.76) (Table 3). The HQs of Cd, As and Pb due to the ingestion of soil, drinking water, crops and fish were higher than 6, which showed that local children near the DCS experienced higher health risks because of Cd, As and Pb pollution. The present results suggested that Cd, As and Pb were the major components of health risks for local children, accounting for 46%, 27% and 20% of the HIt in the exposed area, respectively. Considering both elements and EPs, intake of Cd was the highest via ingestion of rice, accounting for 41% of the HIt in the exposed area. These results were in agreement with the report by Cai et al. (2015). As is generally known, the Itai-itai disease was caused by chronic Cd poisoning because of rice-mediated environmental

Table 2
The contents (mg/kg FW) of heavy metals in the edible parts of plants collected from the exposed area.

Plants	Edible tissue	Cd	Cu	Pb	As
Radish	Roots	0.11 ± 0.09a	2.12 ± 1.93a	0.01 ± 0.01a	0.05 ± 0.05ab
Carrot	Roots	0.16 ± 0.10a	3.63 ± 1.79b	0.02 ± 0.01a	0.02 ± 0.01a
Ipomaea	Tubers	0.13 ± 0.07a	5.36 ± 2.28bc	0.04 ± 0.01a	0.02 ± 0.02a
Celery	Shoots	0.15 ± 0.05a	1.58 ± 0.49a	0.04 ± 0.01a	0.11 ± 0.04b
Lettuce	Shoots	0.23 ± 0.18ab	4.02 ± 1.76b	0.13 ± 0.04b	0.23 ± 0.12c
Red cabbage	Shoots	0.11 ± 0.11a	3.87 ± 3.12b	0.02 ± 0.01a	0.03 ± 0.02a
Pakchoi	Shoots	0.31 ± 0.19b	6.13 ± 3.23c	0.05 ± 0.04a	0.07 ± 0.05b
Cabbage	Shoots	0.32 ± 0.20b	1.19 ± 0.62a	0.02 ± 0.02a	0.07 ± 0.02b
Rice	Grains	1.87 ± 2.29c	5.69 ± 1.59bc	0.27 ± 0.24c	0.13 ± 0.06bc
Maize	Grains	0.21 ± 0.33ab	6.73 ± 5.28c	0.06 ± 0.06ab	0.09 ± 0.05b

The value shown is mean ± S.D. The different small letters stand for statistical significance at $p < 0.05$ with the t-test.

Table 3
Mean values of HQ, HI and HIt calculated for heavy metals through ingestion of each foodstuff, water or soil.

	Cd		Cu		Pb		As		HI	
	Exp	Ref	Exp	Ref	Exp	Ref	Exp	Ref	Exp	Ref
Rice	12.52	0.33	0.95	0.37	3.60	1.74	3.00	1.56	20.07	4.00
Maize	0.14	0.03	0.11	0.01	0.08	0.04	0.18	0.13	0.51	0.21
Vegetable	0.95	0.10	0.46	0.09	0.43	0.15	1.27	0.54	3.11	0.88
Fish	0.35	0.04	0.21	0.06	1.01	0.32	1.98	0.42	3.55	0.84
Water	0.02	0.01	0.00	0.00	0.06	0.05	1.24	0.27	1.32	0.33
Soil	0.03	0.00	0.03	0.00	0.99	0.30	0.64	0.24	1.69	0.54
HIt	14.01	0.51	1.76	0.53	6.17	2.60	8.31	3.16	30.25	6.80

Exp: exposed area; Ref: reference area.

exposure in Japan in 1960s. In addition, the most seriously Cd-contaminated region was the Jinzu river basin in Japan, where the disease was very endemic (Fu et al., 2008). However, the Cd content (1.87 mg/kg) of rice gain collected from the exposed area in the study was significantly higher than that (0.59 mg/kg) in the Jinzu river basin, Japan (Nogawa et al., 2004), so attention should be paid in those areas near the DCS.

The HQs of each exposure route is shown in Table 3. The HI of each ingestion pathways in the exposed area was in the order of rice (20.07) > fish (3.55) > vegetable (3.11) > soil (1.69) > water (1.32) > maize (0.51) (Table 3). These results suggested that ingestion of crops (rice, vegetable and maize) was the most important EP in the exposed area, accounting for 78% of the total exposure, although there exist various possible EPs of HMs to local children, similar to the phenomenon reported in the Lihe River Watershed of the Taihu Region, China (Chen et al., 2018). Therefore, proper measures are needed to remediate the pollution of soil HMs and to reduce metal transfer from soil to the edible part of crops, especially rice in the exposed area.

5. Conclusions

The results revealed that smelting activities of the DCS in Hubei province without effective environmental management in the past have resulted in the release of large volumes of HMs into the surrounding environment, and caused severe contamination of HMs in the environmental media (including soil, crop, well water, and freshwater fish). Due to the ingestion of soil, drinking water, crops and fish, the local children in smelter-affected area were likely under high health risks, up to 30.25 times higher than the acceptable level of 1, and most risks were resulted from Cd, As and Pb exposure through ingestion of crops. Hence, effective measures on pollution control and environmental management of HMs in those areas near the DCS should be taken.

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Appendix A. Supplementary data

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