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Public health risk of toxic metal(loid) pollution to the population living near an abandoned small-scale polymetallic mine

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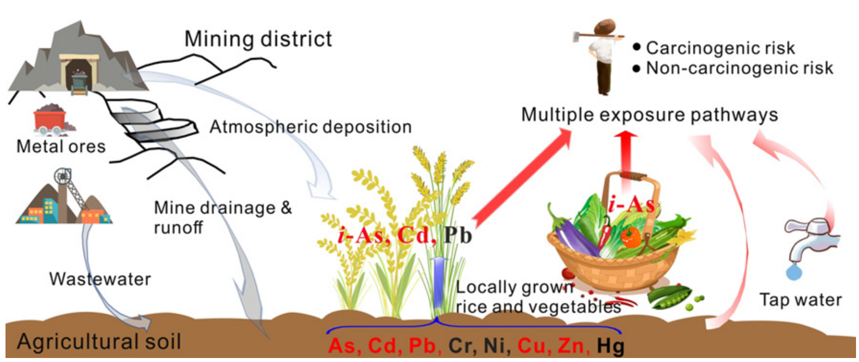
HIGHLIGHTS

- Pollution of environmental media and food crops in a mining area was investigated.
- Comprehensive assessment of the health risk of exposure to metal(loid)s was conducted.
- Arsenic speciation in foods and bioavailability of metal(loid)s were accounted for.
- Inorganic As and Cd in rice and vegetables posed significant non-carcinogenic risk.
- Exposure to inorganic As through rice consumption posed serious carcinogenic risk.

GRAPHICAL ABSTRACT



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ABSTRACT

Small-scale mining activities in many developing countries have caused severe environmental issues to the surrounding areas, which ultimately threatened the health of local populations. Based on detailed characterization of the local drinking water and surface soil, as well as foodstuffs, this study comprehensively assessed the public health risk of toxic metal(loid)s to the population living in three villages surrounding an abandoned small-scale polymetallic mine in southern China. The agricultural soils contained elevated levels of Cu, Zn, As, Cd, and Pb, which originated from the mining district, and as expected, the locally cultivated rice and vegetables were contaminated by As, Cd, and Pb to varying extents. Arsenic occurred in both inorganic and organic forms in the rice and vegetables, with inorganic As (*i*-As) accounting for 82.2% (45.4–100%) and 94.7% (65.2–100%) of the total As contents in rice and vegetables, respectively. Results of health risk assessment indicate that the residents in the impacted villages had serious non-carcinogenic and carcinogenic risk. Dietary exposure to *i*-As and Cd through rice and vegetable consumption was the primary cause of non-carcinogenic risk, while *i*-As intake was the dominant contributor of carcinogenic risk. These findings suggest that significant environmental pollution by toxic metal(loid)s could result from small-scale metal mines, even after being abandoned, and the accumulation of the toxic metal(loid)s in food crops could pose significant health risk to the local residents. Immediate actions should be taken to discourage them from consuming the locally produced food crops, while long-term control measures for containment of toxic metal(loid) pollution are being developed, and high priority should be given to the remediation of Cd and As in the contaminated soils.

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1. Introduction

Risk to human health from exposure to toxic metal(loid)s in contaminated areas continues to be an issue of grave concern in the developing countries in recent years (Abbas et al., 2017; L. Chen et al., 2018; Irshad et al., 2019; Ji et al., 2013; Sharma et al., 2018; Yousaf et al., 2016a). Chronic exposure to toxic metal(loid)s, which interferes the functioning of cell components, such as structural proteins, enzymes, and nucleic acids, may cause various negative human health effects (Hough et al., 2004; Nachman et al., 2018). For instance, exposure to inorganic As (*i*-As) can lead to an increased risk of skin, bladder, and lung cancer, and cause non-cancer diseases, including dermal lesions, peripheral neuropathy, and cardiovascular disease, while chronic intake of Cd can result in bone fractures, prostatic proliferative lesions, kidney dysfunction, and hypertension (Zukowska and Biziuk, 2008). Excessive intake of Pb may cause anemia, gastrointestinal, colic, and central nervous system symptoms, and damage the skeletal, enzymatic, endocrine, and immune systems as well (Nieboer et al., 2013). In general, the health risk mainly arises from chronic exposure to toxic metal(loid)-contaminated food crops, drinking water, and soil (L. Chen et al., 2018). Previous studies have demonstrated that, besides occupational exposure or passive exposure to metal(loid)-bearing particles by inhalation around some industrial sites, consumption of contaminated food crops is the most important route of toxic metal(loid) exposure in humans (Bermudez et al., 2011; Huang et al., 2016; Khan et al., 2008; Nachman et al., 2018). In addition, consumption of water contaminated by toxic metal(loid)s and direct exposure to contaminated soils (via ingestion, dermal contact, and inhalation) can also pose potentially detrimental risk (Lin et al., 2018; Mahfooz et al., 2019).

Non-ferrous metal ore mining can release large amounts of toxic metal(loid)s into the surrounding environment, even long after the cessation of mining activities (Ji et al., 2013; Liu et al., 2010; Sun et al., 2018). The abandoned mining areas are often left with huge amounts of tailings, often in unconfined piles and ponds, which could serve as long-term sources of toxic metal(loid) pollution (Li et al., 2014; Sun et al., 2018). Fine grains of mine tailings and toxic metal(loid)s leached out of the tailings could be easily transported to adjacent farmland soils and streams with surface runoff during and after rainfall, as well as mine drainage (Cheng et al., 2009; Liu et al., 2010; Wang et al., 2019). Cultivation of food crops in soils contaminated by toxic metal(loid)s would result in their excessive accumulation in the edible parts of the plants (Sharma et al., 2018). Consequently, consumption of such grains and vegetables could pose potentially significant health risk to the residents living in the vicinity of the mining areas.

Rice is the staple food for more than half of the world's population, and its consumption has long been recognized as a major source of As exposure for the general population (Kumarathilaka et al., 2019; Meharg et al., 2009; Sommella et al., 2013; Yin et al., 2019; Zhu et al., 2008). Arsenic in rice occurs in both inorganic and organic forms, with *i*-As being much more toxic than the organic ones (Donohue and Abernathy, 1999; Goldenthal, 1971). Inorganic As species, including arsenite (As(III)) and arsenate (As(V)), are non-threshold class 1 carcinogen (IARC, 2012). Typically, As(III), As(V), and dimethylarsinic acid (DMA) are the predominant As species in rice grains (Afroz et al., 2019; Ma et al., 2016; Meharg et al., 2009; Narukawa et al., 2008), while monomethylarsonic acid (MMA) is rarely detected, and arsenobetaine (AsB) and arsenocholine (AsC) are almost undetectable (Ma et al., 2017a). Unfortunately, *i*-As is usually the predominant As species found in the grains of rice cultivated in southern China (Ma et al., 2017a; Zhu et al., 2008). It has also been found that *i*-As is the dominant As species in vegetables, usually accounting for >90% of the total As (Ahmed et al., 2016; Jia et al., 2019; Ma et al., 2017b). Thus, quantification of the total contents of As and characterization of the speciation of As in rice and vegetable are important for accurate assessment of the human health risk through dietary exposure.

In this study, the toxic metal(loid) pollution in the area surrounding an abandoned small-scale polymetallic mine (the Yaoposhan mine), which is located in the remote mountainous region of Guangdong province in southern China, and the corresponding health risk to the local residents were investigated. This area was ideal to demonstrate the impact of mining and related activities on toxic metal(loid) pollution and human health due to the lack of any other major sources of toxic metal(loid) pollution, except vehicular emissions (the area has a low-traffic-volume road) and agrochemicals used on farmlands. With rather low-income levels compared to the populations living in the Pearl River Delta, the local residents maintain a rice-heavy diet and eat primarily homegrown rice and vegetables. It is well known that rice is much more efficient at assimilating As and Cd into its grains than other staple cereal crops (e.g., wheat and corn) (Grant et al., 2008; Meharg et al., 2013; Meharg et al., 2009). Therefore, long-term consumption of the locally grown rice could potentially pose high health risk to the residents living in the area.

Extensive studies have been conducted on assessing the public health risk of exposure to toxic metal(loid)s, while most of them only took a single exposure pathway or certain toxic metal(loid) species into consideration (Bose-O'Reilly et al., 2010; Yousaf et al., 2016b; Joseph et al., 2015; Praveena and Omar, 2017). Little attention has been paid to the combined health risk of exposure to multiple toxic metal(loid)s through multiple pathways. Nevertheless, the public are commonly exposed to toxic metal(loid)s through one or more of the following pathways, including consumption of drinking water, rice, wheat, vegetables, various kinds of meats and seafood, and inhalation of metal(loid)-containing particulates. Furthermore, the speciation of As has not received sufficient attention in the assessment of health risk from dietary exposure to As contained in foodstuffs (L. Chen et al., 2018; Sawut et al., 2018). Generally speaking, toxic metal(loid)s in various orally ingested media/matrices may not be completely absorbed by the human body to become physiologically available to the target tissues (Asante, 2017). Thus, it is important to consider the bioavailability of toxic metal(loid)s when assessing their human health risk. However, only few studies had incorporated this in the exposure calculations (Augustsson et al., 2018; Islam et al., 2014; Li et al., 2017; Li et al., 2016; T. Li et al., 2018). To accurately assess the health risk of toxic metal(loid)s to the residents in the Yaoposhan mine area, all the relevant exposure pathways, including consumption of rice, vegetables, and drinking water, as well as exposure to the soil through oral ingestion, dermal contact, and inhalation, were fully considered in this study. In addition, speciation of As in the rice and vegetables, and the bioavailability of toxic metal(loid)s in different exposure pathways were also taken into account in the health risk assessment. As a consequence, the assessment results can accurately reflect the health risk of the local residents. The pathway and toxic metal(loid) that contributed most to the health risk for the local residents were also identified. The findings can provide useful information for control and risk management of toxic metal(loid) pollution in the Yaoposhan mine area, and other similar metal mining areas as well.

2. Materials and methods

2.1. Sample collection

Intensive open cast mining of lead and zinc ores occured at multiple sites at the Yaoposhan polymetallic mine (24°31′16″N, 113°04′29″E; Fig. 1) between 2012 and 2014. This mine has been abandoned since then, although ores were still excavated by local villagers at several spots. Chashan (A), Xuwu (B), and Wulian (C) are three sparsely populated rural villages located downhill of the mining district, and they are administratively subordinated to Dabu town, Shaoguan city, Guangdong province of China. Climatic conditions and topographic information of this area have been reported in our previous work (Sun et al., 2018). A total of 320 surface soil samples (0–10 cm), together with

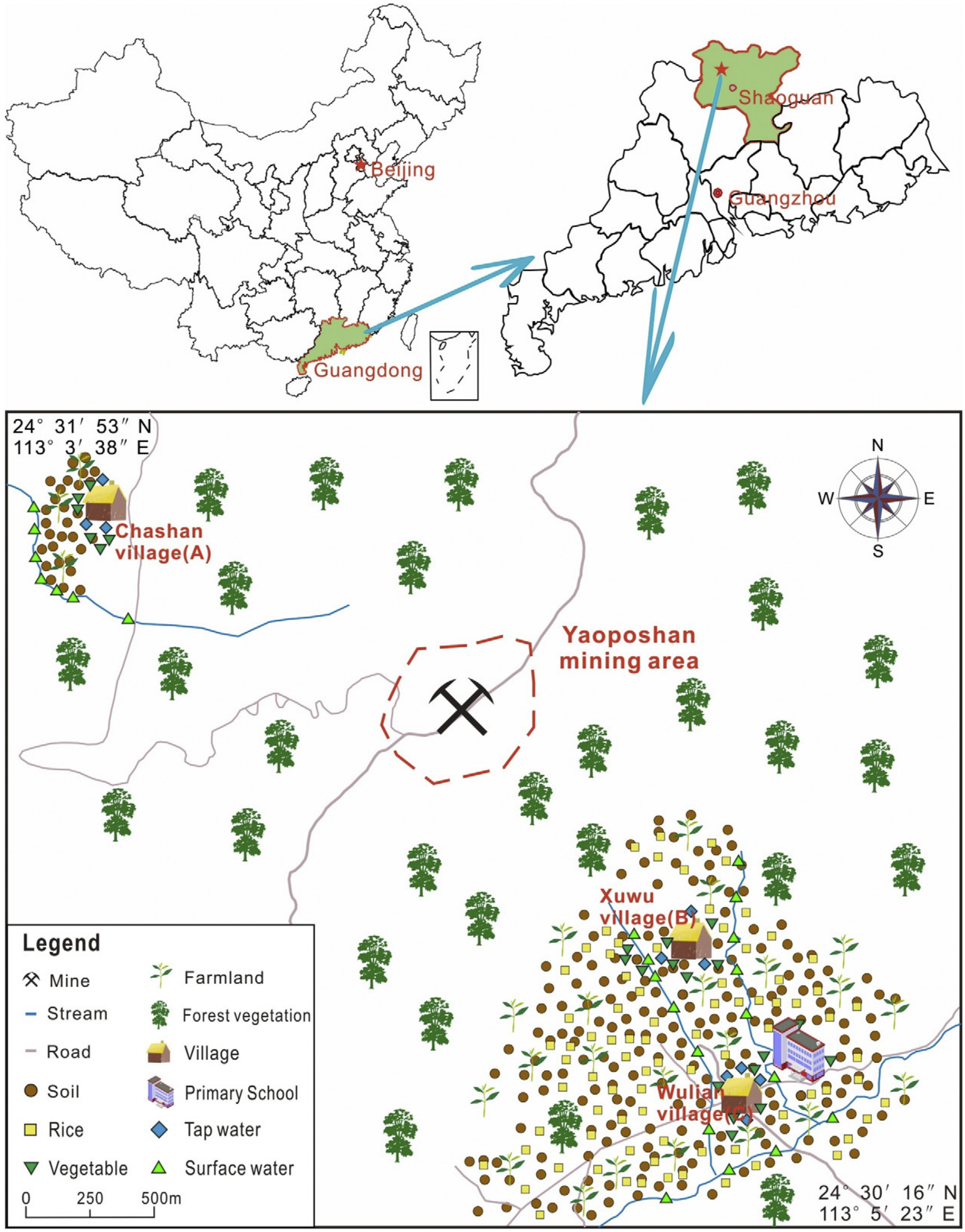

Fig. 1. Schematic illustration of the Yaoposhan mine area and the sampling sites.

155 rice samples and 254 vegetable samples were collected from the three villages and a reference village located 5 km away from the mining district, which was not subjected to the influence of the mining activities at the Yaoposhan mine, between November 2015 and May 2018. Samples of surface water ($n = 23$) were also collected from the local streams, which originate from the mining district and flow through the farmlands of the villages (Fig. 1). In addition, 10 tap water samples were collected from local households, and 8 tap water samples were collected from the households in the reference village. Surface soil samples from the farmlands of the three villages were collected in approximate grids of 50 m by 50 m (Fig. 1). Rice cultivation in village A ceased five years ago due to water deficiency, and the rice purchased from Dabu town was consumed by its residents. Thus, samples of rice purchased randomly from the markets in Dabu town were used to

represent the rice consumed by the residents of village A. All the other rice and vegetable samples from the three villages were collected from local farmlands. For comparison, samples of farmland soils, tap water, rice, and vegetables were also collected from the reference village. Additional details on sample collection and pretreatment are presented in the Supplementary data.

2.2. Measurements of total contents of toxic metal(loid)s

Accurately weighted soil samples (~0.2 g) were digested following the procedure used in our previous study (Sun et al., 2018). Powdered rice and vegetable samples (~0.4 g) were transferred into 50 mL digestion vessels with perfluoroalkoxy alkane (PFA) liners and added with 2 mL of concentrated HNO_3 (70% v/v, BV-III) and 2 mL of H_2O_2 (30% v/v, BV-III). After pre-digestion at room temperature in a fume cupboard for an hour, the vessels were sealed and put in a MARS 6 microwave system (CEM, Matthews, NC, USA). The digestion temperature was raised from room temperature to 120 °C in 10 min and held for 5 min, raised to 160 °C in 5 min and held for 10 min, then raised to 180 °C in 5 min and held for 10 min. After cooling, the digested solutions were diluted to 50 mL with ultrapure water and stored at 4 °C prior to analysis. All the surface water samples, tap water samples, and the digestion solutions obtained from the total digestion were filtered through a 0.22-μm syringe filter, and the digestion solutions were diluted when necessary. The concentrations of Cr, Ni, Cu, Zn, As, Cd, and Pb in these samples were determined by a NexION 350D inductively coupled plasma-mass spectrometer (ICP-MS, PerkinElmer, USA). The total Hg contents in tap water (~0.1 g), surface soil (~0.05 g), rice (~0.1 g), and vegetable (~0.1 g) samples were analyzed by a DMA-80 direct mercury analyzer (Milestone, Italy). It should be noted that the contents of toxic metal(loid)s in the vegetable samples were measured as dry weight, while those on wet weight basis were calculated based on their water contents. For quality assurance/quality control (QA/QC), blanks, at least one of the three soil standard reference materials (GSS6, GSS7, GSS16 from the Chinese Academy of Geological Sciences), and at least one of the four rice or vegetable standard reference materials (GSB21, GSB25, GSB26, GSB27 from the Chinese Academy of Geological Sciences) and duplicated samples were routinely analyzed in each batch.

2.3. Arsenic speciation analysis

The speciation of As in approximately 30% of the rice samples and 20% of the vegetable samples from each village (sampled randomly) were analyzed. Powdered rice (~0.4 g) or dried vegetable (~0.5 g) samples were weighed into 50 mL polytetrafluoroethylene (PTFE) extraction vessels and added with 10 mL of 2% v/v HNO_3. The As species were first extracted from the rice and vegetable samples in closed vessels in a MARS 6 microwave system at 90 °C for 20 min (Jia et al., 2019; Ma et al., 2017b; Rasheed et al., 2018; Zhu et al., 2008). After cooling down to room temperature, the extracts were transferred into 50 mL polyethylene centrifuge tubes and centrifuged at 4000 rpm for 15 min, then the supernatants were filtrated with 0.22-μm syringe filters. The filtrates (~1.5 mL) were stored in 2 mL brown sample vials at 4 °C in the dark and analyzed within 24 h. Four As species, including As(III), As(V), DMA, and MMA, were separated using a Hamilton PRP-X100 anion exchange chromatographic column (250 × 4.1 mm, 10 μm, Reno, NV, USA). Their contents in the extracts were then quantified on an Altus A10 high-performance liquid chromatograph (HPLC, PerkinElmer, USA) coupled with ICP-MS (HPLC-ICP-MS) (Jia et al., 2019). The mobile phase consists of (a) 30 mM $(NH_4)_2HPO_4$ at pH 5.8 (adjusted with dilute HNO_3 solution) and (b) water for the elution of As species. The sample injection volume was 20 μL, and the flow rate of eluent was 1 mL/min. The concentrations of As species in rice and vegetable samples were determined by five-point calibration (0, 10, 20, 50, and 100 μg/L of As) established with mixed standard solutions, which were prepared from single standard solutions of As(III) and As (V) (SPEX, Metuchen, USA), and MMA and DMA (O2Si, Charleston, USA). It is worth noting that the sum of As species obtained from the extraction might not match exactly with the total As content determined after microwave-assisted digestion for the same rice or vegetable sample due to the inevitable occurrence of analytical errors and experimental errors. In spite of this, the sums of As species extracted from rice and vegetable samples and determined by HPLC-ICP-MS agree well with the total As contents determined by ICP-MS after total digestion (94.6 ± 15.5%) in this study.

2.4. Geoaccumulation index

The geoaccumulation index (I_{geo}), which was originally introduced by Müller (1969) for the assessment of toxic metal(loid) contamination of river bottom sediments, has been widely employed to assess the contamination level of toxic metal(loid)s in soils (Ali et al., 2017; Rehman et al., 2020). It can be calculated as:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \quad (1)$$

where C_n is the measured concentration (mg/kg) of toxic metal(loid) in soil, and B_n is its corresponding geochemical background value in the soil of Guangdong province (Table S1). The constant 1.5 is adopted due to the natural fluctuation of baseline data and very small anthropogenic influence (Loska et al., 2004).

2.5. Public health risk assessment

The residents of the three villages surrounding the mining district are potentially at risk from exposure to toxic metal(loid)s through the pathways of ingestion, dermal contact, and inhalation. The carcinogenic and non-carcinogenic health risk of toxic metal(loid) exposure was assessed using the models developed by the U.S. Environmental Protection Agency (USEPA). In general, human dietary exposure to toxic chemicals in food depends both on the consumption patterns and their contents in the food consumed. The estimated average daily ingestion rate (ADI_{ing}) of a particular toxic metal(loid) (mg/kg BW/day) is calculated as:

$$ADI_{ing} = \frac{C_i \times IngR \times EF \times ED}{BW \times AT} \quad (2)$$

where C_i is the content of the toxic metal(loid) in the tap water, rice, vegetable, or soil (mg/kg); *IngR* represents the daily intake rate (L/day or kg/day) of tap water, rice, vegetable, or soil (via accidental ingestion). *EF* is the exposure frequency, *ED* is the exposure duration, *BW* is the body weight of the exposed individual, *AT* is the average effective time.

Toxic metal(loid)s in soils could also pose health risk to humans via the exposure routes of dermal absorption (ADI_{dermal}) and inhalation through mouth and nose (ADI_{inh}). The doses of toxic metal(loid) exposure through these two pathways were assessed following the guidelines given in the Exposure Factors Handbook developed by the USEPA for health risk assessment (USEPA, 1989). Accordingly, the average daily intake rates of toxic metal(loid)s through dermal absorption and inhalation are calculated as:

$$ADI_{dermal} = C_i \times \frac{SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (3)$$

$$ADI_{inh} = C_i \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \quad (4)$$

where *SA*, *AF*, and *ABS* are the exposed skin surface area, adherence factor, and dermal absorption factor, respectively, while *InhR* and *PEF* are the inhalation rate and emission factor of soil particles, respectively. The values and units of these parameters used in this study are summarized in Table S2. It is worth noting that it is better to use the concentrations of toxic metal(loid)s (ng/m^3) in the atmospheric particulate matter and the corresponding reference concentrations (RfC, ng/m^3) when assessing the health risk of residents living near active metal mines through inhalation exposure (USEPA, 1989).

The non-carcinogenic risk of toxic metal(loid) exposure was assessed by the hazard index (HI), which is the sum of the hazard quotient (HQ) of the toxic metal(loid)s evaluated via different exposure pathways:

$$HI = \sum HQ_{i,j} = \sum \frac{ADI_{i,j}}{RfD_{i,j}} \tag{5}$$

where $HQ_{i,j}$ indicates the hazard quotient of toxic metal(loid) i through the exposure pathway j, and $ADI_{i,j}$ is the average daily intake rate of toxic metal(loid) i through the exposure pathway j, and $RfD_{i,j}$ is the corresponding reference dose. The exposed population is unlikely to suffer obvious adverse health effects when $HI < 1$, while detrimental health effects may occur when HI is above 1 (MEP, 2014; USEPA, 2002).

The carcinogenic risk was assessed with the incremental lifetime carcinogenic risk ($ILCR$), which represents the probability of an individual developing cancer over a lifetime from the exposure to toxic metal(loid)s with carcinogenicity (USEPA, 1989). $ILCR$ can be calculated as:

$$ILCR = \sum ADI_{i,j} \times CSF_{i,j} \tag{6}$$

where $CSF_{i,j}$ is the cancer slope factor of toxic metal(loid) i through the exposure pathway j. The CSF for i-As (oral exposure) issued by the Integrated Risk Information System (IRIS) (last revision in 1998) was 1.5 $(mg/kg\ BW/day)^{-1}$, which corresponds to skin cancer (USEPA, 1988a). Based on the results from recent epidemiological research, the USEPA has proposed a CSF value of 25.7 $(mg/kg\ BW/day)^{-1}$ for lung and bladder cancer induced by i-As (oral exposure) in 2010 (USEPA, 2010). The cancer susceptibility is known to have dependence on ethnicity and region, while there are obvious differences in physical characteristics between the Chinese and U.S. populations. As a result, the CSFs established based on the U.S. population were adjusted with an ethnicity factor of 0.86 in the health risk assessment for Chinese population. This adjustment factor had been used in evaluating the lung cancer risk of polycyclic aromatic hydrocarbon and i-As exposure for Asian populations (Hu et al., 2017a; Shen et al., 2014). $ILCR$ values above 1×10^{-4} are viewed as unacceptable and represent a high probability of developing cancer, while those below 1×10^{-6} are considered safe and unlikely to cause significant carcinogenic effect (USEPA, 1989). The recommended values of RfD and CSF for other investigated toxic metal(loid)s through different exposure pathways are presented in Table S3.

To account for the uncertainty of the parameters used in health risk assessment, including the contents of toxic metal(loid)s in different media, body weights of local residents, ingestion rates of drinking water and foodstuffs, and human variability in genetic polymorphism, Monte Carlo simulations were conducted to estimate the probability distributions of HI and $ILCR$ using Matlab software (R2018a). The measured contents of toxic metal(loid)s in the soil and foodstuff samples

Table 1

Summary of toxic metal(loid) concentrations (geometric mean ± standard deviation) in the surface water, tap water, soil, vegetable (wet weight), and rice samples from the Yaoposhan mine area and the reference village.

Sample type	Location	n	Cr	Ni	Cu	Zn	As	Cd	Pb	Hg
Surface water[a] (μg/L)	Local streams	23	29.8 ± 2.04	–	$2.30 \times 10^{-2} \pm 0.111$	14.0 ± 70.6	1.18 ± 6.78	15.9 ± 1.14	$3.17 \times 10^{-2} \pm 9.93 \times 10^{-2}$	–
Tap water (μg/L)	Local households	10	0.380 ± 1.63	0.176 ± 0.135	0.768 ± 1.24	3.14 ± 7.91	$0.218 \pm 8.88 \times 10^{-2}$	$3.90 \times 10^{-2} \pm 5.82 \times 10^{-2}$	0.235 ± 0.711	$0.406 \pm 9.82 \times 10^{-2}$
	Reference village	8	$4.59 \times 10^{-2} \pm 4.53 \times 10^{-2}$	$3.31 \times 10^{-2} \pm 2.11 \times 10^{-2}$	$2.00 \times 10^{-2} \pm 4.68 \times 10^{-2}$	72.5 ± 20.1	$0.183 \pm 9.59 \times 10^{-2}$	$2.58 \times 10^{-2} \pm 3.22 \times 10^{-2}$	$7.87 \times 10^{-3} \pm 3.53 \times 10^{-2}$	$6.43 \times 10^{-2} \pm 3.20 \times 10^{-2}$
Soil (mg/kg)	Village A	79	71.9 ± 19.1	24.8 ± 15.1	96.5 ± 28.2	214 ± 81.4	47.9 ± 10.8	0.648 ± 0.353	265 ± 114	$0.202 \pm 6.82 \times 10^{-2}$
	Village B	115	87.7 ± 18.4	47.8 ± 7.38	100 ± 41.4	248 ± 99.6	48.5 ± 21.9	0.995 ± 0.836	238 ± 260	$0.196 \pm 4.54 \times 10^{-2}$
	Village C	118	84.1 ± 18.2	41.9 ± 8.45	164 ± 74.5	411 ± 149	89.3 ± 40.4	1.85 ± 1.35	595 ± 350	$0.197 \pm 5.37 \times 10^{-2}$
	Reference village	8	99.0 ± 9.10	35.2 ± 3.10	77.2 ± 27.0	134 ± 7.86	75.0 ± 29.3	0.492 ± 0.131	91.5 ± 7.63	$0.143 \pm 2.69 \times 10^{-2}$
Leafy vegetable (mg/kg)	Village A	29	0.496 ± 0.813	0.298 ± 0.425	0.748 ± 0.158	4.05 ± 2.33	$8.45 \times 10^{-2} \pm 0.703$	$4.54 \times 10^{-2} \pm 2.55 \times 10^{-2}$	0.328 ± 0.558	$1.38 \times 10^{-3} \pm 5.20 \times 10^{-4}$
	Village B	43	0.386 ± 0.702	0.314 ± 0.411	0.842 ± 0.587	3.02 ± 1.75	$4.16 \times 10^{-2} \pm 0.401$	$6.75 \times 10^{-2} \pm 7.79 \times 10^{-2}$	0.224 ± 0.200	$1.21 \times 10^{-3} \pm 7.59 \times 10^{-4}$
	Village C	35	0.361 ± 0.353	0.260 ± 0.235	0.948 ± 0.698	4.98 ± 3.54	$6.55 \times 10^{-2} \pm 0.196$	$8.89 \times 10^{-2} \pm 0.170$	0.236 ± 0.218	$1.07 \times 10^{-3} \pm 4.06 \times 10^{-4}$
	Reference village	29	0.291 ± 0.306	0.178 ± 0.184	0.888 ± 0.577	2.82 ± 1.50	$1.39 \times 10^{-2} \pm 2.55 \times 10^{-2}$	$3.70 \times 10^{-2} \pm 3.39 \times 10^{-2}$	$5.20 \times 10^{-2} \pm 0.228$	$7.29 \times 10^{-4} \pm 3.66 \times 10^{-4}$
Non-leafy vegetable (mg/kg)	Village A	63	$6.73 \times 10^{-2} \pm 6.08 \times 10^{-2}$	0.142 ± 0.108	0.675 ± 0.354	2.09 ± 1.54	$3.53 \times 10^{-3} \pm 5.89 \times 10^{-3}$	$6.83 \times 10^{-3} \pm 7.28 \times 10^{-3}$	$2.37 \times 10^{-2} \pm 1.83 \times 10^{-2}$	$1.05 \times 10^{-4} \pm 1.91 \times 10^{-5}$
	Village B	14	$2.90 \times 10^{-2} \pm 4.58 \times 10^{-2}$	0.235 ± 0.227	0.817 ± 0.265	1.66 ± 1.23	$2.01 \times 10^{-3} \pm 3.61 \times 10^{-3}$	$1.95 \times 10^{-2} \pm 2.40 \times 10^{-2}$	$1.54 \times 10^{-2} \pm 3.39 \times 10^{-2}$	$7.50 \times 10^{-5} \pm 5.47 \times 10^{-5}$
	Village C	18	$5.03 \times 10^{-2} \pm 6.94 \times 10^{-2}$	$8.12 \times 10^{-2} \pm 7.73 \times 10^{-2}$	0.739 ± 0.230	1.36 ± 0.979	$5.55 \times 10^{-3} \pm 2.23 \times 10^{-2}$	$7.71 \times 10^{-3} \pm 2.25 \times 10^{-2}$	$4.26 \times 10^{-2} \pm 9.81 \times 10^{-2}$	$1.00 \times 10^{-4} \pm 3.00 \times 10^{-4}$
	Reference village	23	$7.17 \times 10^{-2} \pm 5.95 \times 10^{-2}$	$9.61 \times 10^{-2} \pm 7.05 \times 10^{-2}$	0.360 ± 0.300	1.34 ± 0.781	$9.66 \times 10^{-3} \pm 2.46 \times 10^{-2}$	$2.53 \times 10^{-3} \pm 6.10 \times 10^{-3}$	$1.02 \times 10^{-2} \pm 1.06 \times 10^{-2}$	$1.46 \times 10^{-4} \pm 6.36 \times 10^{-5}$
Rice (mg/kg)	Village A	23	1.62 ± 1.77	1.43 ± 1.17	2.82 ± 0.333	10.5 ± 0.541	$0.145 \pm 3.66 \times 10^{-2}$	$8.14 \times 10^{-2} \pm 3.01 \times 10^{-2}$	$6.44 \times 10^{-2} \pm 0.181$	$3.07 \times 10^{-3} \pm 1.52 \times 10^{-3}$
	Village B	53	0.155 ± 0.411	0.338 ± 0.431	4.19 ± 0.803	13.6 ± 1.03	0.165 ± 0.104	0.149 ± 0.172	0.156 ± 0.159	$4.40 \times 10^{-3} \pm 6.35 \times 10^{-3}$
	Village C	69	0.106 ± 0.149	0.349 ± 0.313	4.65 ± 0.860	14.3 ± 1.37	0.172 ± 0.139	0.603 ± 0.500	0.386 ± 0.401	$4.23 \times 10^{-3} \pm 6.79 \times 10^{-3}$
	Reference village	10	0.673 ± 1.28	0.475 ± 0.227	2.58 ± 0.268	11.0 ± 1.01	$0.178 \pm 5.36 \times 10^{-2}$	$0.183 \pm 9.11 \times 10^{-2}$	$5.32 \times 10^{-2} \pm 6.24 \times 10^{-2}$	$5.65 \times 10^{-3} \pm 1.91 \times 10^{-3}$

[a] The concentrations of toxic metal(loid)s in surface water are expressed as arithmetic mean ± standard deviation because the metal(loid)s occurred in some samples at levels below the detection limits.

apparently followed log-normal distributions (Fig. S1), thus the means and standard deviations (STDs) based on the log-transformed data were used in the uncertainty analysis. The proportions of *i*-As in the total As contents of rice and vegetable samples fitted well with normal distributions (Fig. S2), and the means and STDs of these distributions (Table S4) were taken. The average daily consumption rates of drinking water, rice, and vegetables for adults in rural areas of Guangdong province were 1.7 L, 372 g, and 274 g, respectively (Duan et al., 2015; Ma et al., 2005). They were assumed to follow normal distributions, and the STDs were set as 40% of the means (Table S2), based on the results of a recent diet investigation in Guangdong province (Huang et al., 2013). The ingestion rate of soil for adults was 20 mg/day as recommended by the USEPA, and the estimated STD of log-transformed daily soil ingestion rate was 0.4 (USEPA, 1989). The mean body weight of adults in the three villages was set at 57.0 kg, and the estimated STD of log-transformed body weight was 0.18, based on the results of Guangdong province in the latest national survey (Duan et al., 2015). In general, the estimates of chemical-specific *RfD* and *CSF* for toxic metal(loid) exposure (oral) could have uncertainty spanning perhaps an order of magnitude, while their variability could be adequately accounted for based on the USEPA's documents (USEPA, 1987a, 1987b, 1987c, 1988a, 1988b, 1995, 2004, 2005). The STDs of the log-transformed *RfDs* and *CSF*s for the toxic metal(loid)s concerned in this study are listed in Table S3.

The oral bioavailability of toxic metal(loid)s in drinking water was assumed to be 100%. Based on the relevant data on toxic metal(loid)s reported in health risk assessment literature, the bioavailability of As (*i*-As in food), Cd, and Pb in soil and foodstuffs were assumed to follow log-normal distributions, with means and STDs summarized in Table S5. The bioavailability of other toxic metals was conservatively assumed to be 100% due to lack of reliable data. The variability of genetic polymorphisms can be accounted for by an adjustment factor, which was assumed to follow a log-normal distribution (mean: 1; STD: 0.65) (Hu et al., 2017a; Shen et al., 2014) On the basis of the probability distributions of the above variables, those of *HI* and *ILCR* of toxic metal(loid) exposure for the residents living in the villages surrounding the mining district of the Yaoposhan mine were assessed with Monte Carlo simulations (10,000 runs).

3. Results and discussion

3.1. Toxic metal(loid) contents in local surface soils and tap water

Table 1 summarizes the basic statistics on the contents of toxic metal (loid)s in the surface soil and tap water samples collected from the reference village and the three villages surrounding the mining district. In the mining district of the Yaoposhan mine, intensive mining operations occurred only briefly before its abandonment, while primitive ore mining still took place at several spots. These past and current mining activities contributed to the elevated metal(loid) contents in the agricultural soils surrounding the mining district. The geometric mean contents of Cu, Zn, As, Cd, and Pb in the farmland soils of the villages in the vicinity of the mine were in the ranges of 96.5–164, 214–411, 47.9–89.3, 0.648–1.85, and 265–595 mg/kg, respectively, which are approximately 1.5–8 times of the corresponding risk screening criteria (50, 200, 30, 0.3, and 70 mg/kg, respectively) for soil contamination of agricultural lands in China (MEP, 2018). The geometric mean contents of Cr, Ni, and Hg in the farmland soils of the three villages surrounding the mining district were in the ranges of 71.9–87.7, 24.8–47.8, and 0.196–0.202 mg/kg, respectively, which were below the corresponding risk threshold values of 150, 60, and 0.5 mg/kg (MEP, 2018). It is worth noting that the geometric mean contents of Cu, As, Cd, and Pb in the soil samples collected from the reference village also exceeded the corresponding soil quality standards. Fig. 2 shows the contamination levels of toxic metal(loid)s in the agricultural soils of different villages based on I_{geo}. Surface soils in the farmlands of the reference village were moderately to heavily

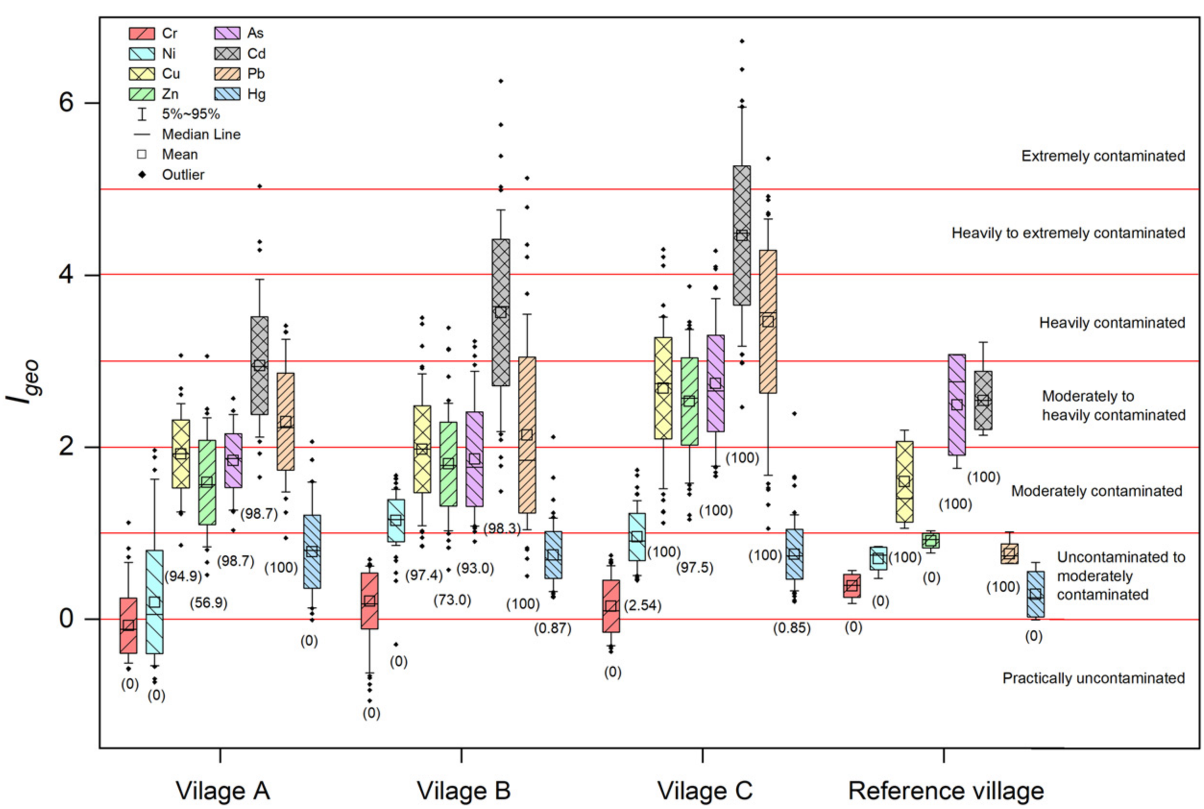

Fig. 2. Boxplots of the geoaccumulation index (I_{geo}) for toxic metal(loid)s in the soils from farmlands surrounding the mining district of the Yaoposhan mine and in those from farmlands of the reference village, along with the classification of contamination level based on the values of I_{geo}. The numbers in the parentheses are the percentages of soil samples with contents of toxic metal(loid)s exceeding the corresponding soil environmental quality standards (MEP, 2018).

contaminated by Cu, As, and Cd. The elevated regional geochemical background levels of these metal(loid)s are not surprising given the occurrence of lead-zinc polymetallic deposit at the Yaoposhan mine. Farmland soils near the Yaoposhan mine were more contaminated by Cu, Zn, Cd, Pb, and As (village C) than those of the reference village, indicating they had received significant exogenous input of toxic metal (loid)s. Due to the varying deposition of fine tailings carried by surface runoff (during rainfall events) arising from their topographic difference (Sun et al., 2018), the farmlands in the three villages were contaminated to different degrees by toxic metal(loid)s, decreasing in the order of C > B > A. The results of Pearson's correlation matrix (Table S6) suggest that Cu, Zn, As, Cd, and Pb in the farmlands surrounding the mining district probably originated from the same sources. Based on the fact that this area had no other major sources of toxic metal(loid) pollution, together with the results of Pearson's correlation matrix, it is reasonable to infer that the higher contents of toxic metal(loid)s in the farmland soils closer to the mining district were associated with the mining and related activities. The above results also suggest that soils in the Yaoposhan mine area were naturally enriched with Cu, As, Cd, and Pb, while mining activities had significantly elevated the contents of Cu, Zn, As, Cd, and Pb in the impacted farmlands.

The geometric mean contents of Cr, Ni, Cu, Zn, As, Cd, and Pb in the stream water flowing through the farmlands of the three villages were 29.8, 8.17×10^{-2}, 2.30×10^{-2}, 14.0, 1.18, 15.9, and 3.17×10^{-2} μg/L, respectively. The geometric mean concentration of Cd in the stream water exceeded the national standard for surface water of Class V (10 μg/L), which is applicable to the water bodies for agricultural irrigation and landscaping, by 60%. That is, the stream water was actually not suitable for irrigating the farmlands due to the excessive levels of Cd. Unfortunately, the paddy fields in the vicinity of the Yaoposhan mine have long been irrigated by the local stream water, which could contribute to the accumulation of Cd and other toxic metal(loid)s in the soils (and the food crops grown in them as well).

The geometric mean concentrations of Cr, Ni, Cu, Zn, As, Cd, Pb, and Hg in the tap water samples of the three villages were 0.380, 0.176, 0.768, 3.14, 0.218, 3.90×10^{-2}, 0.235, and 0.406 μg/L, respectively (Table 1). These levels were far below the corresponding standards for drinking water issued by the National Health Commission of China, the World Health Organization, and the Maximum Contaminant Levels (MCLs) set by the USEPA (Table S7). The tap water of the three villages was supplied by a local drinking water treatment plant (treatment processes could easily remove most toxic metal(loid)s). The tap water of the reference village was supplied by a drinking water treatment plant in Dabu town, and the levels of toxic metal(loid)s (except Zn) were lower than those in the drinking water of the three villages. The drinking water in both the reference village, which was not impacted by the mining activities, and in the villages surrounding the mining district was safe for consumption (with respect to toxic metal(loid)s), despite the occurrence of significant toxic metal(loid) pollution in the local streams flowing through the three villages.

3.2. Toxic metal(loid) contents in foodstuffs

With the farmlands and surface water both contained elevated levels of toxic metal(loid)s, rice and vegetables grown on the farmlands would likely have excessive accumulation of toxic metal(loid)s. The accumulation of toxic metal(loid)s in the edible tissues of the food crops could bring food safety concerns. As shown in Table S8, the geometric mean contents of toxic metal(loid)s in nearly all vegetable samples collected from the three villages surrounding the mining district were below the respective safety limits specified in the National Food Safety Standard of China (NHC, 2017). A few leafy vegetables had As, Cd, and Pb contents exceeding the food safety limits, while the toxic metal (loid) contents in all non-leafy vegetables were within the acceptable ranges. The geometric mean contents of As in water spinach ($n = 4$) grown on the farmlands in village A, and Cd in leaf lettuce ($n = 6$) grown on the farmlands in village C were 2.04 and 0.447 mg/kg (wet weight), respectively, far above the national food safety standards of 0.5 and 0.2 mg/kg for As and Cd in leafy vegetables, respectively. The leafy vegetables produced in this area also had elevated levels of Pb. The Pb contents in Pakchoi (550 ± 658 μg/kg, $n = 15$) collected in village A, leek (350 ± 87.0 μg/kg, $n = 6$) and water spinach (645 ± 65.5 μg/kg, $n = 13$) collected in village B, and water spinach collected in village C (405 ± 329 μg/kg, $n = 5$) and the reference village (582 ± 172 μg/kg, $n = 6$) were all above the food safety limit of 0.3 mg/kg. Overall, it appears that leafy vegetables had higher contents of toxic metal(loid)s than non-leafy ones, which is consistent with the findings of previous studies (X. Li et al., 2018). As expected, the vegetables grown on the farmlands impacted by the mining and related activities had significantly higher contents of toxic metal(loid)s compared to those grown on the farmlands of the reference village (Table 1 and Fig. 3). The levels of As, Cd, and Pb in vegetables grown on the farmlands of the three villages surrounding the mining district were comparable to those in other industrial areas, and were higher than those in the vegetables grown in soils with no apparent toxic metal(loid) contamination (Table S9). Vegetables grown in contaminated soils could accumulate more toxic metal(loid)s than those cultivated in clean soils, although they could still meet the food safety standards in general.

Rice grown on the farmlands of villages B and C had significant enrichment of As, Cd, and Pb. In particular, the geometric mean contents of Cd and Pb in the rice from village C were 0.603 and 0.386 mg/kg, respectively, approximately 3 and 2 times higher than the allowable levels of 0.2 mg/kg for both Cd and Pb. Rice grown on the farmlands of reference village also contained rather high levels of As and Cd, which could be explained by their high contents in the farmland soils. The rice consumed by the residents of village A, which was probably cultivated on farmlands close to the Yaoposhan mine area, had relatively high contents of As, but rather low contents of Cd and Pb. Besides the elevated levels of As in the environmental media (soils and irrigation water), the relatively high levels of As in all rice samples could be attributed to the high As accumulation potential of rice (Davis et al., 2017). In contrast, the contents of Cd and Pb in the rice samples varied widely (Fig. 3), which was probably related to the varying contamination levels of these metals in farmland soils and irrigation water in the area. The contents of Hg in >96.5% of all the rice samples were below the food safety limit of 20 μg/kg, with little difference between the villages. In general, the Hg contents in rice are low across China, except for the rice from a few Hg mining areas (Luo et al., 2019; Zhao et al., 2019).

3.3. Speciation of As in rice and vegetables

Fig. S3 shows HPLC-ICP-MS chromatograms of As species in the extracts of representative rice and vegetable samples, along with that of a mixed standard. Arsenic species occurred primarily in the forms of As(III) and As(V) in vegetables, while DMA and MMA were rarely detected. In comparison, As(III), As(V), and DMA were the predominant As species in rice, while MMA was almost non-detectable. Table 2 shows that *i*-As accounted for 82.2% (45.4–100%) and 94.7% (65.2–100%) of the total As in the rice and vegetables grown in the Yaoposhan mine area, respectively, which are similar to those found in rice and vegetables from other parts of China and other countries, except the rice produced in the U.S., which was dominated by DMA (Zhu et al., 2008; Zhao et al., 2013). The proportion of *i*-As in total As in rice was generally less than that of vegetables, while the mean proportion of *i*-As in the rice from village A (68.0%) was approximately 20% lower than those in the rice from villages B (86.5%) and C (93.4%) (Table S4). The proportions of *i*-As in total As in the vegetables grown on the farmlands of the three villages surrounding the mining district and those from the reference village were roughly comparable. Fig. 4 shows that the contents of *i*-As in both rice and vegetables increased linearly with increases in their total As contents. In particular, an excellent linear relationship ($R^2 = 0.99$) was observed between *i*-As contents and total As

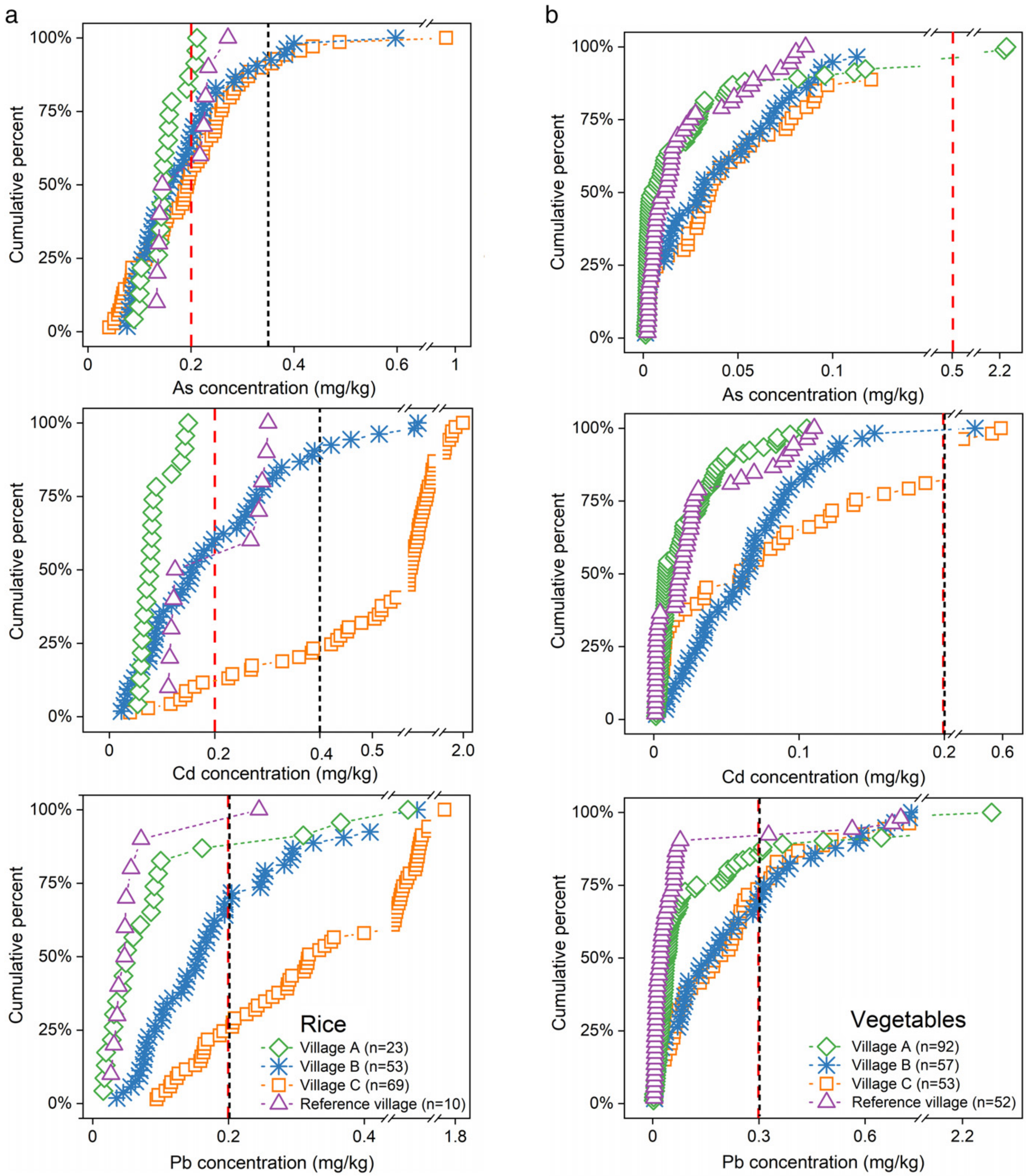

Fig. 3. Empirical cumulative distribution of the contents of toxic metal(loid)s (As, Cd, and Pb) in (a) rice and (b) vegetables (wet weight) from the three villages in the Yaoposhan mine area and the reference village. The red and black vertical dash lines represent the threshold values for As (inorganic), Cd, and Pb in the National Food Safety Standard of China (NHC, 2017) and the General Standard for Contaminants in Food adopted by the Codex Alimentarius Commission (JECFA, 2019), respectively.

contents in vegetables, which allows estimation of the contents *i*-As in them based on the contents of total As. Based on the results of As speciation, it is estimated that 13% of rice samples from villages B and C had *i*-As contents exceeding the national food safety limit of 0.2 mg/kg, while none of the rice samples (and vegetable samples as well) from village A and the reference village contained *i*-As at levels above this standard.

3.4. Health risk of exposure to toxic metal(loid)s through multiple pathways

The elevated levels of toxic metal(loid)s in the farmland soils impacted by mining and related activities pose potential human health risk through the exposure pathways of ingestion, dermal contact, and

Table 2
Comparison of the contents of As species (μg/kg) in the rice and vegetables (wet weight) from the Yaoposhan mine area with those in rice and vegetables from other areas in China and the rest of world.

Sample type and location			Total As	As(III)	As(V)	DMA	MMA	i-As (%)
Rice	Yaoposhan mine area (this study) (n = 47)	Mean ± SD	178 ± 56.2	115 ± 34.6	37.0 ± 43.6	24.8 ± 26.8	1.26 ± 2.96	82.2 ± 11.9[i]
		Min–max	8.00–280	60.0–232	N/D–225	N/D–133	N/D–18.0	45.4–100
	Hunan province[a] (n = 43)	Mean ± SD	129 ± 46.2	107 ± 33.2	4.70 ± 5.10	9.60 ± 6.40	0.300 ± 0.500	91.9[i]
		Min–max	50.2–253	44.5–198	N/D–23.8	1.40–30.6	N/D–2.80	
	China[b] (n = 160)	Mean	87.0	54.0[h]		26.0		62.1
		Min–max	11.0–186	9.00–133[h]		3.00–98.0		
	Bangladesh[c] (n = 144)	Mean	130	80.0[h]				61.5
		Min–max	20.0–330	10.0–210[h]				
	Italy[c] (n = 38)	Mean	150	110[h]				73.3
		Min–max	70.0–330	70.0–160[h]				
	U.S.[c] (n = 163)	Mean	250	100[h]				40.0
		Min–max	30.0–660	50.0–150[h]				
	U.S. (bought in Beijing)[d] (n = 3)	Mean ± SD	329 ± 21.0	91.7 ± 11.4	41.7 ± 9.50	137 ± 4.04		40.4 ± 2.61
		Min–max	308–350	79.0–101	32.0–51.0	133–141		38.6–43.4
Vegetable[e]	Yaoposhan mine area (this study) (n = 50)	Mean ± SD	23.0 ± 15.6	7.33 ± 5.28	10.8 ± 7.94	0.998 ± 1.33	0.279 ± 0.527	94.7 ± 7.72[i]
		Min–max	2.20–66.9	0.270–27.2	0.390–31.2	N/D–5.87	N/D–2.78	60.3–100
	Changsha[f] (n = 42)	Mean	224	81.8	117	1.22		90.8[i]
		Min–max	71.3–403	23.4–222	38.1–176	N/D–6.10		75.1–100
	Bangladesh[g] (n = 21)	Mean	287	276[h]				96.1
		Min–max	110–520					

N/D - not detected.
[a] Data from Ma et al. (2016).
[b] Data from L. Chen et al. (2018).
[c] Data from Meharg et al. (2009).
[d] Data from Zhu et al. (2008).
[e] Contents of total As and As species (wet weight).
[f] Data from Ma et al. (2017b).
[g] Calculated based on the data from Ahmed et al. (2016).
[h] Content of *i*-As in the rice.
[i] The percentage of *i*-As in total As does not match very well with the sum of As(III) and As(V) divided by total As due to the existence of errors in the results obtained with both extraction and digestion.

inhalation, while the enrichment of toxic metal(loid)s, particularly As, Cd, and Pb, in the rice and vegetables grown on the farmlands inevitably increases the dietary intake of these metal(loid)s, which also increases the health risk of the local residents. Fig. 5a shows that all adult residents of village C had *HI* values above the serious risk level due to the exposure to toxic metal(loid)s (Cr, Ni, Cu, Zn, As, Cd, Pb, and Hg) through various pathways. Furthermore, exposure to toxic metal(loid)s through drinking water and soils (via three pathways) posed insignificant non-carcinogenic risk to the local residents, while rice and vegetable consumption was the primary contributor of the non-carcinogenic risk (Fig. 5b). In particular, all the adult residents in village C had *HI* values above the risk reference level through rice consumption and approximately half of them had *HI* values above the risk reference level due to vegetable consumption. Fig. S4a to c shows that the residents of villages A and B, and the reference village also suffered significant non-carcinogenic risk from toxic metal(loid) exposure through consumption of rice and vegetables, although the rice consumed by the residents of village A was not produced locally. The contribution ratios of exposure to toxic metal(loid)s through the media of rice, vegetable, soil, and tap water for the non-carcinogenic risk of the residents living in the vicinity of the mining district were 62.3–86.6%, 8.51–32.9%, 2.37–5.03%, and 0.67–1.97%, respectively.

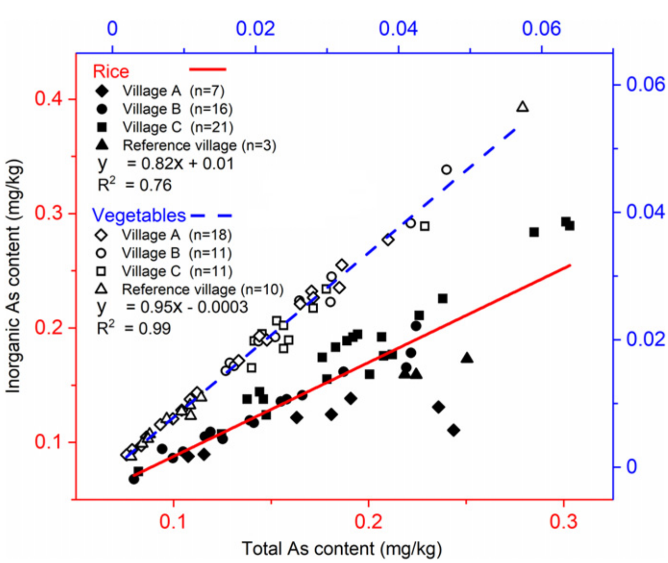

Fig. 4. Correlations between the contents of *i*-As and total As in rice and vegetables (wet weight) from the three villages in the Yaoposhan mine area and the reference village.

Table 3 summarizes the estimated *HQ*s for the residents of village C due to exposure to specific toxic metal(loid) from consumption of rice and vegetables. Among all the toxic metal(loid)s investigated in rice and vegetables, *i*-As and Cd posed the most serious potential health risk, Cu and Pb posed lower health risk, while Cr, Ni, Zn, and Hg posed no risk. For the residents of village C, the non-carcinogenic risk of exposure to *i*-As and Cd through rice and vegetable consumption is comparable with that of the residents' exposure to As and Cd through consuming rice and vegetables grown on metal(loid)-contaminated soils in other parts of China and other countries (H. Chen et al., 2018; X. Li et al., 2018; Luo et al., 2011; Ma et al., 2016; Praveena and Omar, 2017). These results suggest that dietary exposure to toxic metal(loid)s from consumption of rice and vegetables grown on the farmlands surrounding the mining district could pose significant non-carcinogenic risk to the local residents, which was contributed mainly by *i*-As and Cd in the rice.

Fig. 5c shows the cumulative probability distributions of *ILCR* of As and Pb exposure from accidentally ingested soil particles, drinking water, and lifetime consumption of locally grown rice and vegetables for the adult residents of village C. The comprehensive *ILCR* from dietary exposure to Pb through various pathways was below the acceptable level of 10^{-4} for the adult residents of village C (also see Table S10). The *ILCR* (skin cancer) for the adult populations in village C from

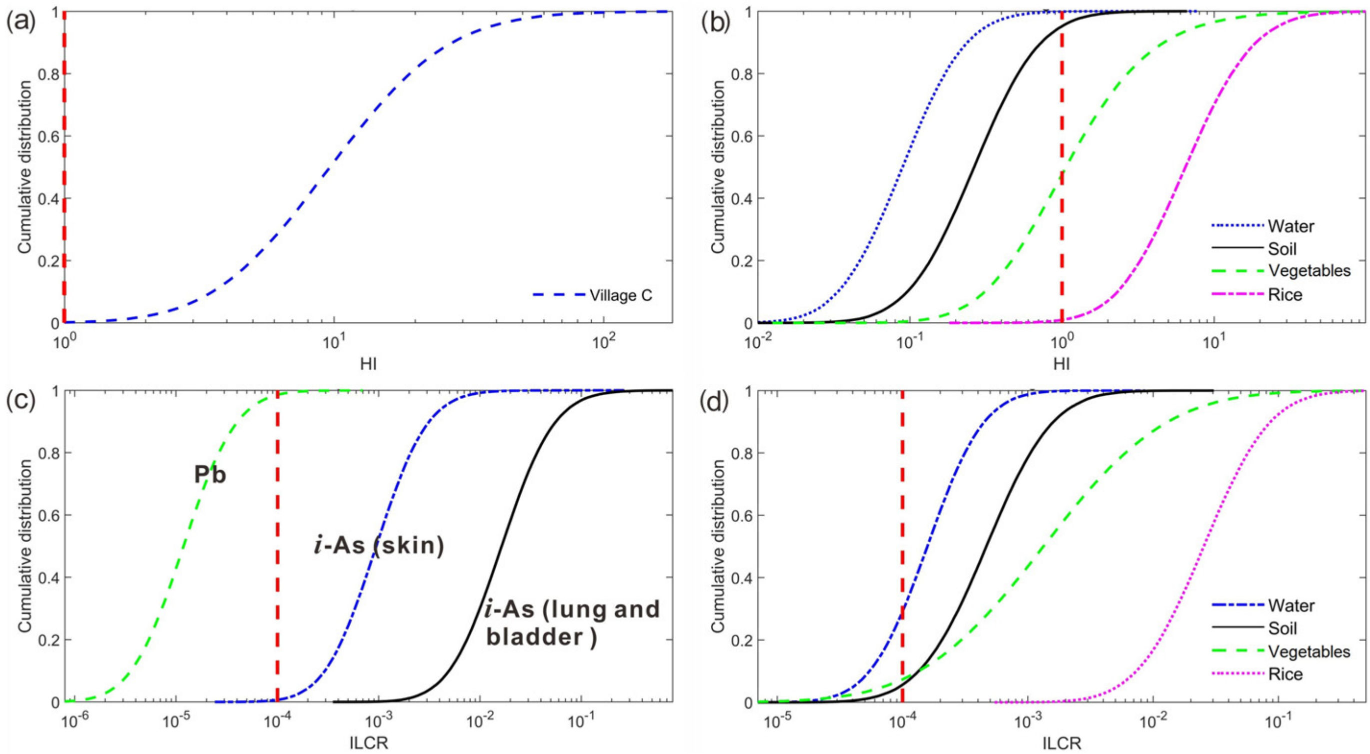

Fig. 5. Non-carcinogenic and carcinogenic risk from toxic metal(loid)s through various exposure pathways for the adult residents of village C in the Yaoposhan mine area: (a) Cumulative probability distribution of *HI* of toxic metal(loid)s; (b) breakdown of the cumulative probability distribution of *HI* from toxic metal(loid) exposure contributed by different media; (c) cumulative probability distribution of *ILCR* of Pb and *i*-As; (d) breakdown of the cumulative probability distribution of *ILCR* (lung and bladder cancer) from *i*-As exposure contributed by different media.

exposure to *i*-As through multiple pathways ranged from 1.2×10^{-4} to 9.4×10^{-3} (Table S10), which is considered serious. The *ILCR* for lung and bladder cancer was 17 times higher than that of skin cancer due to the much higher cancer slope factor of *i*-As for the former (Hu et al., 2017b; USEPA, 2010) Fig. 5d shows the breakdown of lung and bladder cancer risk from *i*-As exposure for the adult residents of village C contributed by different media. As expected, the cancer risk was primarily contributed by consumption of the locally produced rice and vegetables. The carcinogenic risk of As through dermal contact with soil particles, and that of As and Cd through inhalation of the soil particles were below the acceptable level for the residents of village C, which had the most serious toxic metal(loid) pollution in the farmland soils (Fig. S6).

The residents of villages A and B, and the reference village also had serious risk of lung and bladder cancer and skin cancer due to the exposure to *i*-As through rice and vegetable consumption (Fig. S5a–c). It is noted that although the residents of village A and the reference village did not consume rice grown on farmlands impacted by the mining activities, they also had serious health risk due to the exposure to *i*-As through rice consumption. These results suggest that the rice grown on the farmlands in the entire Dabu town might not be suitable for human consumption (probably due to elevated geochemical background of As, Fig. 2), which deserves significant attention. Overall, the residents living in the vicinity of the mining district would face serious non-carcinogenic and carcinogenic risk, particularly lung and bladder

Table 3
Statistical information for the estimated *HQs* of dietary exposure to toxic metal(loid)s from consumption of locally produced rice and vegetables for the adult residents of village C based on the results of Monte Carlo simulations.

Food type	Toxic metal(loid)	P1[a]	P5[a]	P10[a]	P25[a]	P50[a]	P75[a]	P90[a]	P95[a]	P99[a]
Rice	Cr	9.1×10^{-5}	1.9×10^{-4}	2.9×10^{-4}	5.7×10^{-4}	1.2×10^{-3}	2.6×10^{-3}	5.0×10^{-3}	7.5×10^{-3}	1.6×10^{-2}
	Ni	1.3×10^{-2}	2.6×10^{-2}	3.7×10^{-2}	6.7×10^{-2}	1.3×10^{-1}	2.5×10^{-1}	4.5×10^{-1}	6.4×10^{-1}	1.2
	Cu	1.7×10^{-1}	2.7×10^{-1}	3.5×10^{-1}	5.4×10^{-1}	8.8×10^{-1}	1.4	2.2	2.8	4.5
	Zn	7.1×10^{-2}	1.1×10^{-1}	1.5×10^{-1}	2.2×10^{-1}	3.6×10^{-1}	5.7×10^{-1}	8.7×10^{-1}	1.1	1.8
	i-As	1.5×10^{-1}	3.2×10^{-1}	4.6×10^{-1}	8.8×10^{-1}	1.8	3.7	6.9	1.0×10^{1}	2.1×10^{1}
	Cd	1.1×10^{-1}	2.5×10^{-1}	3.9×10^{-1}	8.0×10^{-1}	1.8	3.9	8.1	1.2×10^{1}	2.8×10^{1}
	Pb	1.9×10^{-2}	4.4×10^{-2}	6.7×10^{-2}	1.4×10^{-1}	3.0×10^{-1}	6.7×10^{-1}	1.4	2.1	4.5
	Hg	7.7×10^{-3}	1.7×10^{-2}	2.5×10^{-2}	4.9×10^{-2}	1.1×10^{-1}	2.3×10^{-1}	4.5×10^{-1}	6.9×10^{-1}	1.4
Vegetable	Cr	4.4×10^{-5}	1.2×10^{-4}	2.2×10^{-4}	5.5×10^{-4}	1.5×10^{-3}	4.4×10^{-3}	1.1×10^{-2}	1.9×10^{-2}	5.5×10^{-2}
	Ni	3.1×10^{-3}	6.9×10^{-3}	1.1×10^{-2}	2.2×10^{-2}	4.7×10^{-2}	1.1×10^{-1}	2.1×10^{-1}	3.3×10^{-1}	7.3×10^{-1}
	Cu	1.7×10^{-2}	3.0×10^{-2}	4.1×10^{-2}	6.8×10^{-2}	1.2×10^{-1}	2.1×10^{-1}	3.5×10^{-1}	4.8×10^{-1}	8.5×10^{-1}
	Zn	4.4×10^{-3}	9.3×10^{-3}	1.4×10^{-2}	2.8×10^{-2}	5.9×10^{-2}	1.2×10^{-1}	2.5×10^{-1}	3.7×10^{-1}	7.8×10^{-1}
	i-As	3.0×10^{-3}	1.0×10^{-2}	2.0×10^{-2}	6.0×10^{-2}	2.1×10^{-1}	7.2×10^{-1}	2.2	4.3	1.5×10^{1}
	Cd	9.1×10^{-4}	3.4×10^{-3}	7.0×10^{-3}	2.3×10^{-2}	8.5×10^{-2}	3.2×10^{-1}	1.0	2.1	7.7
	Pb	2.4×10^{-3}	6.5×10^{-3}	1.1×10^{-2}	2.8×10^{-2}	7.6×10^{-2}	2.1×10^{-1}	5.1×10^{-1}	8.8×10^{-1}	2.4
	Hg	2.5×10^{-4}	7.0×10^{-4}	1.2×10^{-3}	3.1×10^{-3}	8.6×10^{-3}	2.4×10^{-2}	6.1×10^{-2}	1.1×10^{-1}	3.0×10^{-1}

[a] P1 (1st percentile), P5 (5th percentile), P10 (10th percentile), P25 (25th percentile), P50 (50th percentile or median), P75 (75th percentile), P90 (90th percentile), P95 (95th percentile), and P99 (99th percentile).

cancer, from chronic consumption of the rice and vegetables grown on the farmlands impacted by the toxic metal(loid)s released from the mining and related activities in the Yaoposhan mine area.

4. Conclusions

The public health risk of heavy metal(loid) pollution to the residents living in three villages surrounding an abandoned small-scale polymetallic mine in southern China was assessed comprehensively based on consideration of all the relevant exposure pathways, including consumption of foodstuffs (rice and vegetables) and drinking water, as well as exposure to the soils through oral ingestion, dermal contact, and inhalation. The results show that the farmlands surrounding the mining district had been severely contaminated by heavy metal(loid)s, which resulted in pollution of the locally produced rice and vegetables. Health risk assessment revealed that dietary exposure to *i*-As and Cd from rice and vegetable consumption was the primary cause of the serious non-carcinogenic risk to the local residents, while *i*-As was the dominant contributor to the significant carcinogenic risk from lifetime consumption of locally produced rice and vegetables. The results of this study demonstrated that small-scale mining activities could cause serious toxic metal(loid) pollution of the surrounding environment and ultimately threaten the health of neighboring residents through the soil-plant-human system. As such abandoned small mines are typically located in remote regions, their impact on the environment and human health has not received sufficient attention, and little effort has been made on effective management of the mine tailings and treatment of the mine drainage. With millions of small-scale metal mines exploited in the developing countries, their cumulative impact on public health deserves great attention. Preventing the occurrence of further pollution of the surrounding environment by toxic metal(loid)s from these small mines may be costly and takes time. Nonetheless, human health should be protected by taking immediate actions on stopping the residents in such areas from consuming locally produced rice and vegetables. Local authority could develop rice exchange and purchase programs to ensure local villagers only consume rice that meet the safety standards, and discourage them from eating locally produced vegetables. These measures would help protect the health of residents living in the vicinity of metal mining areas while long-term solutions for the significant toxic metal(loid) pollution problem are being developed.

CRediT authorship contribution statement

Zehang Sun: Conceptualization, Data curation, Methodology, Visualization, Writing - original draft, Writing - review & editing. **Yuanan Hu:** Conceptualization, Software, Project administration, Resources, Supervision, Writing - original draft. **Hefa Cheng:** Conceptualization, Funding acquisition, Supervision, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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