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Chronic impact of an accidental wastewater spill from a smelter, China: A study of health risk of heavy metal(loid)s via vegetable intake

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ABSTRACT

Chronic impact will last from a sudden pollution accident, however, potential adverse effects of heavy metal (loid)s are overlooked when pollution decreased during years of equilibration. Here, we assessed the potential health risks of heavy metal(loid)s via intake of vegetables from fields affected by the smelting wastewater spill eight years later, basing on site-specific target hazard quotient (STHQ) and cancer risk (SCR) models. Results showed kohlrabi, lettuce and garlic had significant high concentrations of Sb (10.4 mg kg^{-1}), Pb (21.0 mg kg^{-1}), Cd (6.49 mg kg^{-1}), and Zn (441 mg kg^{-1}), and sweet potato and garlic enriched high levels of As (19.6 mg kg^{-1}) and Cu (14.1 mg kg^{-1}), respectively. Transfer factors of metal(loid)s from soil to plants were enhanced by high soluble metal(loid) concentrations, and Sb, As, Pb and Cd in most edible tissues exceeded the contamination limitations for food in China and FAO/WHO. Chinese cabbage had significant high STHQ of As (adult 9.31 and child 19.8) and Sb (adult 0.76 and child 1.61) ($p < 0.05$), and the highest STHQ of Cd (adult 1.41 and child 3.02) was in lettuce, whereas the highest STHQ of other elements from vegetables were below 1. However, the non-carcinogenic risks based on total STHQ values of these vegetables were several times higher than the acceptable level of 1. In addition, the total SCR values at 5% were hundreds times of safety level of 5.0×10^{-5} set by International Commission on Radiological Protection. Considering food frequency and metal(loid) levels, long-term consumption of local vegetables, especially lettuce and Chinese cabbage, are likely to increase non-carcinogenic and carcinogenic (e.g. As and Cd) health risks. Child's health risk of toxic elements was far greater than adult. This study might serve as a case study of long-term adverse impact for other pollutant incidents. People should pay attention to human health through food chain, and the government should solve the outstanding environmental problems that harm the health of the masses.

1. Introduction

Soil metal(loid) contamination aggravated by metalliferous mining and smelting activities is a major environmental concern worldwide (Bhuiyan et al. 2010; Popescu et al. 2013; Ettler, 2016; Khan et al. 2017; Liu et al. 2018; Rai et al. 2019). In 2008, the breaking of the wastewater treatment systems at the Jinhai Metallurgy Chemical Industry (a lead and antimony smelter, Hechi, China) during storms spilled million tons of wastewater rich in heavy metal(loid)s to the surroundings, and about 60 ha farmlands in 4 villages suffered from serious pollution of Zn, Cu, As, Pb and Sb (Tserenpil and Liu, 2011; Yuan and Liu, 2011). This accident became one of the ten most severe pollution events in the last decade in China (Lu et al. 2015). The smelter was then shut down and soil remediation programs were implemented for the affected areas after the accident, while about 2 ha croplands in front of the smelter were abandoned due to flooded months by wastewater. Several years after the accidental spill, vegetation is spontaneously recovered under the humid subtropical climate even if no remediation method was used in the 2 ha flooded fields. Villagers started to grow vegetables for self-consumption since 2014, however significant high concentrations of water-soluble Sb, As, Pb, Cd, Zn and Cu were also measured in the 0–20 cm top layer soils (Yuan et al., 2017), indicting high plant-available metal(loid) concentrations. Therefore, long-term pollution of the accidental spill remains.

Soil-to-plant transfer of metal(loid)s is one major pathways of human exposure to soil contamination, which causes subsequent/

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Abbreviations;

THQ	Target Hazard Quotient
STHQ	Site-Specific Target Hazard Quotient
HI	Hazard Index
CR	Cancer Risk
CR_n	Total Cancer Risk
SCR_n	Site-Specific CR_n
EDI	Estimated Daily Intake
SEDI	Site-Specific Estimated Dietary Intake
TF	Transfer Factor
EF	Enrichment Factor
EF_i	Exposure Frequency
ED	Exposure Duration
Bw	Body Weight
AT	Averaging Time
F_i	Food Frequency
RfD_o	Oral Reference Doses
SF_o	Slope Factor
ICRP	International Commission on Radiological Protection

chronic adverse effects (Khan et al. 2017; Rehman et al. 2017; Mi et al. 2019). Vegetables are the primary exposure pathways of heavy metal (loid)s to human (Khan et al. 2008; Cao et al. 2010; Salazar et al. 2012; Boussen et al. 2013; Uddh-Soderberg et al. 2015; Huang et al. 2017),contributing about 70–90% of the total metal intake (Martorell et al. 2011; Khan et al. 2015). Hence the accumulation of heavy metal (loid)s in agricultural soils subsequently impaired health risks to the inhabitants at the tail end of food chain (Douay et al. 2013; Akoto et al. 2015; Khan et al. 2015; Lu et al. 2015; Rai et al. 2019). Cadmium, As and Pb frequently and Sb sometimes found in foodstuffs are listed as potential carcinogens by USEPA (1989) and EU (EFSA, 2010), and even as essential elements, Zn and Cu are toxicity to humans and animals at excessive concentration in food and feed plants (Kabata-Pendias and Mukherjee, 2007; Rai et al. 2019). The prolonged consumption of heavy metal(loid)-contaminated food at elevated levels may cause serious systemic health problems (e.g. cardiovascular, nervous, kidney and bone diseases) (Jarup, 2003; Kabata-Pendias and Mukherjee, 2007; Garcia-Leston et al. 2010).

Health risks of heavy metal(loid)s resulting from regular mining activities is well studied (Boussen et al. 2013; Khan et al. 2015; Lu et al. 2015; Huang et al. 2017; Rai et al. 2019), whereas chronic impacts of mining spill incidents remains poorly studied, as long term toxicity existed even if pollution decreased in soil over time (Romero-Freire et al. 2016). However, there is much debate between the increased risk of human health and the consumption of vegetables cultivated in contaminated sites (Augustsson et al. 2018). Therefore, the information of heavy metal(loid)s in homegrown vegetables from fields affected by the wastewater spill is needed to identify high exposure of heavy metal (loid)s and to assess the accidental spill's chronic impacts on human health. Meanwhile, toxic metal(loid)s can actually be more harmful for child than adult, due to their physiological susceptibility and vulnerability (Man et al. 2010; Gallagher et al. 2015; Khan et al. 2015; Cao et al. 2016). In addition, in the reality, people consume multiple foods, however, most of the ingestion risk assessments focused on assumption of local food self-sufficiency (Ma et al. 2012; Li et al. 2015), and seldom considered the relevant daily food frequency (Fi) at least the majority crops (Augustsson et al. 2018).

Although vegetation has recovered naturally in areas polluted by heavy metal(loid)s, there might be still strong health risks. Here we measured the concentrations of Sb, As, Pb, Cd, Zn and Cu in vegetables and corresponding soils in fields suffered from wastewater flooding eight years later, and then assessed the associated potential chronic health risks to local adult and child through consumption of these crops based on relevant daily food frequency. The target hazard quotients (THQ), hazard index (HI) and cancer risk (CR) were used to assess non-carcinogenic and carcinogenic health risks, respectively.

2. Materials and methods

2.1. Study area

The study area was around a Pb/Sb smelter situated at the suburb of Hechi, northwest Guangxi, China (seen Fig. 1). This area has a humid subtropical climate with average annual temperature of 20.4 °C, a rainfall of 1470 mm, and 180–210 m above sea level. The soil is a leached brown calcareous type. About 2 ha croplands in front of the smelter was flooded by the accidental spill of wastewater for months, and high pollution load of Sb, As, Pb, Cd, Zn and Cu to soils were detected (Tserenpil and Liu, 2011; Yuan and Liu, 2011). As vegetation successful restoration years later, local villagers transformed the polluted fields to croplands for fast growing vegetables.

2.2. Sampling and pre-treatment

Vegetables commonly cultivated and consumed were selected and collected in 2016 from the contaminated croplands around the smelter, including lettuce (*Lactuca sativa* var. *romana* Gars) (n = 7), Chinese cabbage (*Brassica pekinensis*(L.)Rsupr) (n = 6), water spinach (*Ipomoea aquatica* Forsk) (n = 8), garlic (*Allium sativum* L.) (n = 9), sweet potato (*Ipomoea batatas* Lam) (n = 6) and kohlrabi (*Brassica oleracea* L. var. Caulorapa DC.) (n = 5), fruits), which represented the major vegetation types growing in this area, although each kind of vegetable was planted very irregularly. Fresh plant samples were stored in polyethylene bags and placed in a refrigerator at 4 °C, and taken to the laboratory as soon as possible. At laboratory, the samples were rinsed with running water to remove possible adhered particles, and then separated into shoot or aerial part (stem and leaf) and root subsamples after thorough washing with Milli-Q water, and finally freeze-dried to constant weight. The dried samples were ground to a fine powder, packed in paper bags, and stored for analysis. Rhizosphere soils (n = 41) of corresponding vegetables and control soils (n = 3) in a field far away from the smelter were also collected. The soils were also lyophilized to constant weight after

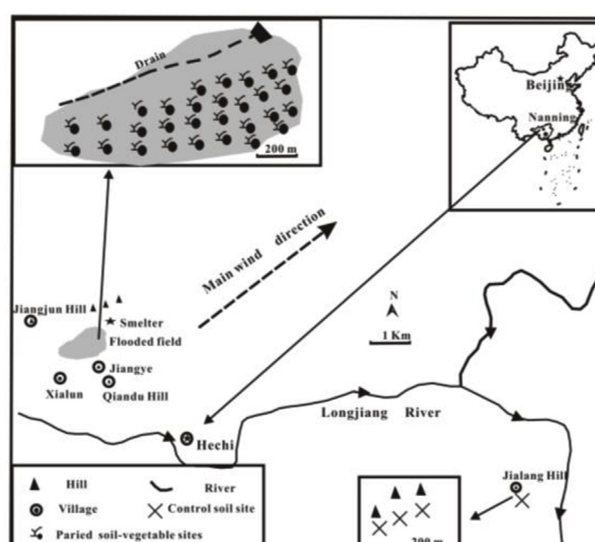

Fig. 1. Location and description of the study area by modified from Yuan et al. (2017).

removing small roots and other debris, and ground by an agate mortar and pestle to pass through 100-mesh nylon sieves before analyses.

2.3. Sample analysis, quality assurance and quality control

Soil and vegetable samples were wet digested with a mixture of concentrated HNO_3–HF–H_2O_2 (Yuan and Liu, 2011) and HNO_3–H_2O_2 (Yuan et al. 2016), respectively. Concentrations of Sb, As, Pb, Cd, Zn and Cu in samples were determined by inductively coupled plasma mass spectrophotometry (ICP-MS).

Precision and accuracy of analysis were assured through repeated analysis of the national standard soil (GBW-07404) and plant samples (GBW-07602). The recovery rates of metals were 95.2–105% and 91.1–113% for standard soil and plant, respectively. Further, each analytical batch contained a blank and a standard solution as a check on instrument performance to assessing contamination and reliability of data. The coefficients of variation of replicate analysis were determined for different determinations for precision of analysis and variations below 10% were considered credible.

2.4. Data analysis

2.4.1. Transfer factor from soil to the edible parts of a vegetable

Soil to plant transfer is one of the major ways for animal and human exposure to heavy metal(loid)s through food (Singh and Prasad, 2015). The transfer factor, or uptake factor, can be used to evaluate the potential capability of plants to transfer metal(loid)s from soil to edible tissues. The TF is expressed as the ratio of metal(loid) concentration in the edible part of plant to corresponding soil metal(loid) concentration ($TF = C_{edible}/C_{soil}$).

2.4.2. Estimated daily intake (EDI) of heavy metals in vegetables

The estimated dietary intake (EDI) (μg kg^{-1} $person^{-1}$ day^{-1}) exposure to metal(loid)s was dependent on metal(loid) concentrations in edible parts of vegetables, daily vegetable consumption, and a period of time (a life time), as well as body weight, which was calculated as follows:

$$EDI = C \times Con \times EF_i \times ED/(Bw \times AT) \quad (1)$$

where C is the average concentration of a heavy metal(loid) in vegetable (mg kg^{-1} dry weight); Con is the ingestion rate of vegetable (g $person^{-1}day^{-1}$), and average daily intakes of vegetables for adult inhabitants and children were 345 and 232 g $person^{-1}day^{-1}$, respectively (Liu et al. 2010a; Khan et al. 2015). EF_i is the exposure frequency (365 days $year^{-1}$); ED is the exposure duration (70 years for adults and 12 years for child); Bw is the average body weight (60 kg for adults and 19 kg for child) (Liu et al. 2010b); AT is the non-carcinogen's averaging time (ED × 365 day/year) (USEPA, 2006; Khan et al. 2015).

According to the food frequency (F_i), Chinese cabbage and lettuce might account for about 60% (30% each) of total consumption of vegetables (Wang et al. 2011), and then other vegetables were considered as 40% daily consumption based on a week dietary survey of the 30 and 42 households in villages of Xialun and Jiangye, respectively (Fig. 1). The total site-specific estimated dietary intake (SEDI) of each metal in each vegetable was the sum of the product of EDI multiplying corresponding F_i ($SEDI = \Sigma ED_i \times F_i$).

2.4.3. Calculation of health risks

Human health risk assessment is widely identified as a way to estimate the nature and probability of adverse health effects in human. Target hazard quotients (THQ) was used to express the potential non-cancer risk for individual heavy metal(loid)s, which was defined as the ratio of the EDI of metals to the reference dose oral (RfD_o) of each metal (loid) (USEPA, 2012), as in the following equation:

$$THQ = EDI/RfD_o \quad (2)$$

The RfD_o values used were 0.4, 1, 1, 300, and 40 μg $kg^{-1}d^{-1}$ for Sb, As, Cd, Zn, and Cu, respectively (USEPA, 2012), due to the US EPA has not yet established RfD_o value for Pb, the one used in this paper was 40 μg $kg^{-1}d^{-1}$ (Huang et al. 2008). Similar to SEDI, the site-specific THQ (STHQ) of each vegetable was expressed as THQ multiplying corresponding F_i ($STHQ = THQ \times F_i$).

The total THQ or hazard index (HI) was expressed the overall potential health risk for non-carcinogenic effects from multiple heavy metal(loid)s, which has been formulated based on the Guidelines for Health Risk Assessment of Chemical Mixtures of USEPA (USEPA, 1989) as follows:

$$HI = \sum THQ = EDI_1/RfD_{o1} + EDI_2/RfD_{o2} + \cdots + EDI_i/RfD_{oi} \quad (3)$$

If TQH (or HI) < 1, no obvious risk is involved, while, if THQ (or HI) ≥ 1, a high risk of non-carcinogenic (nc) effects is implied, and related interventions and protective measurements should be taken. Similarly, site-specific HI of each vegetable was calculated as HI multiplying corresponding F_i ($SHI = \Sigma HI_i \times F_i$).

Due to As and Cd were classified as human carcinogens (Jarup, 2003; Kabata-Pendias and Mukherjee, 2007), to which long-term exposure via different pathways has been verified to increase cancer risk (CR). The annual lifetime excess cancer risk associated with ingestion of metal-contaminated vegetables was assessed using the following formula (Ke et al. 2015).

$$CR = EDI \times SF_o/(L \times 30) \quad (4)$$

where SF_o is a cancer slope factor of different metal for carcinogenic effects, and USEPA (2006) has established SF_o for ingestion only for As and Cd, which is 1.5 and 6.1, respectively. L is the average human longevity (average adult lifetime was considered to be 70 years), and 30 is average number of days per month. Assuming additive effects, total cancer risk (CR_n) was denoting sum CR of each carcinogen. Similarly, site-specific CR_n of each vegetable was calculated as CR_n multiplying corresponding F_i ($SCR_n = \Sigma CR_{ni} \times F_i$). According to the International Commission on Radiological Protection (ICRP), the CR value of 5.0×10^{-5} a^{-1} is generally considered acceptable safe, representing only 5 of 100,000 people may have increased cancer effects (Yuan et al. 2014).

2.5. Statistical analysis

The data were using SPSS 16.0 package (SPSS, USA) for statistically analyzing. One-way ANOVA test (Duncan) and Two-sample t-tests, with a significance level of $P < 0.05$, were employed to examine the statistical significance of the differences of the samples. The data expressed in terms of means, and the figures were present with the mean values and standard errors.

3. Results and discussion

3.1. Concentrations of heavy metal(loid)s and their distribution in vegetables

Heavy metal(loid) concentrations showed variations among different vegetables grown near the smelter (Table S1, supplementary materials). On average, significant high concentrations of Sb, Pb, Cd, and Zn were found in kohlrabi, kohlrabi, lettuce, garlic ($p < 0.05$), at 10.4, 21.0, 6.49, and 441 mg kg^{-1}, respectively. Whereas insignificantly differences of As and Cu were detected in vegetables. The Pb, Cd, Zn and Cu concentrations in vegetables (fresh weight based on 5%–10% water content) were higher than that in Dabaoshan mining areas, Guangdong, China (Zhuang et al. 2009), and Pingle Mn mine area, Guangxi, China (Liu et al. 2018), and metal smelter contaminated sites in Australia (Kachenko and Singh, 2006). The Sb levels in Chinese cabbage and garlic were also comparable to the values in Xikuangshan

(XKS), the world's largest antimony mine area (Wu et al. 2011). In fact, very large range of Sb concentrations (0.004–1400 mg kg^{-1}) were reported in other edible plants (Pierart et al. 2015). Among the vegetation species, lettuce enriched more amounts of Cd and Pb (Zhuang et al. 2009), and kohlrabi and sweet potatoes accumulated higher concentrations of As and Sb, while garlic had significant higher levels of Zn ($p < 0.05$). It has reported leafy vegetables (e.g. lettuce, Chinese cabbage) were considered as potential accumulators of heavy metal (loid)s, without exhibiting any toxicity symptoms when accumulation of heavy metal(loid)s in their tissues (Khan et al. 2015; Huang et al. 2017; Mi et al. 2019). These results indicated that genotype had a determining influence on the bioaccumulation capacity of plants (Alexander et al. 2006; Boussen et al. 2013; Mi et al. 2019).

The concentrations of Sb, As, Pb, Cd, Zn, and Cu (mg kg^{-1}, dw) in the edible parts of different vegetables were presented in Fig. 2. The edible parts were mainly shoots in this study, including sweet potato, whose young shoots are used for human consumption and animal feeding. Compared with total concentrations, great differences were present for each metal concentration in edible parts of vegetables. For Sb, water spinach showed significantly high concentration (2.34 mg kg^{-1}) in shoots than other vegetables ($p < 0.05$), and the lowest Sb was in lettuce shoots (Fig. 2a). Although the total Sb concentration was the highest, insignificant high Sb level was detected in the edible parts of kohlrabi, illustrating Sb was mainly accumulated in kohlrabi root. Nowadays, there are few limited standards of Sb in food, thus we adopted the Australian Food hygiene Standard (1.5 mg kg^{-1}) from the introduction of GB/T 5009.137-2003 (MHPRC, 2003). The Sb levels in water spinach and garlic exceeded this

Table 1
Contents of heavy metal in soil nearby the smelter (mg·kg^{-1}, M ± SD) .

element	Contents of heavy metal in soil (n = 41)	Contents of heavy metal in contrast area (n = 3)	CEQSS[a]	CSQG[b]	EF[c]
Sb	526 ± 139	21 ± 12	10	–	25.1
As	299 ± 135	39 ± 24	25	12	7.67
Pb	1445 ± 156	76 ± 35	600	70	19.0
Cd	24 ± 8	2.0 ± 0.92	0.3	1.4	12.0
Zn	1470 ± 345	26 ± 12	250	200	56.5
Cu	184 ± 124	10 ± 2.5	100	63	18.4

[a] CEQSS = China Environmental Quality Standards for Soil (SEPA, 2008).
[b] CSQG = Canadian Soil Quality Guideline s for the Protection of Environment and Human Health (CCME, 2007).
[c] EF = $C_{sample}/C_{control}$.

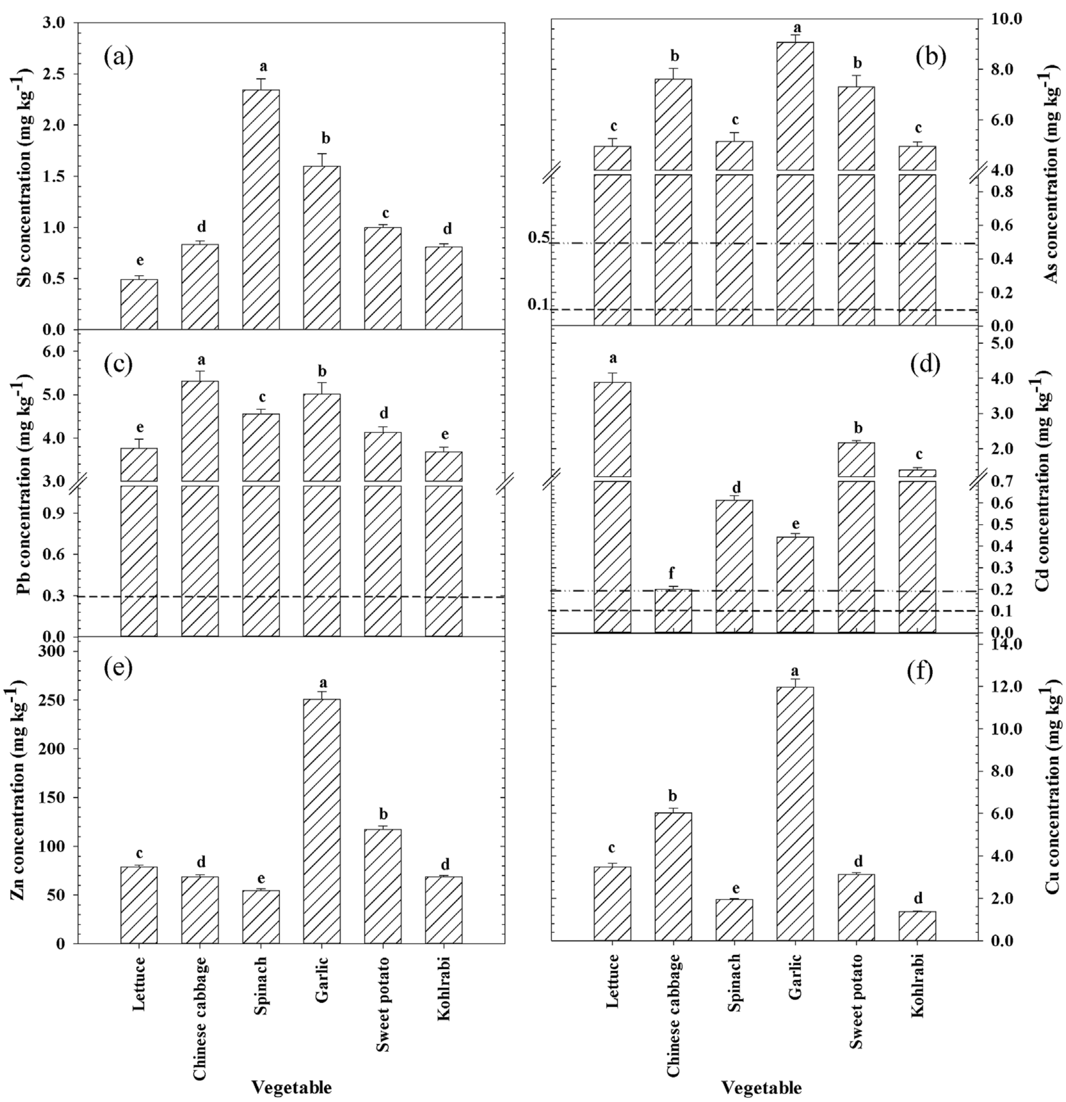

Fig. 2. Concentrations (mg kg^{-1} dW) of metals in the edible parts of different vegetables.
Dash-Dot-Dot line and Short-Dash line stand for tolerance limit of contaminants in food set by SEPA China and WHO/FAO, respectively. Different small letters indicate a significant difference ($p < 0.05$) among different plant species with Duncan's test.

Table 2
The transfer factor of heavy metals from soils to vegetables (M ± SD).

vegetables	Sb (10^{-3})	As(10^{-3})	Pb(10^{-3})	Cd(10^{-2})	Zn(10^{-2})	Cu(10^{-2})
Lettuce	0.91 ± 0.06e	16.6 ± 1.03c	2.61 ± 0.15e	16.2 ± 1.08a	5.37 ± 0.12c	1.89 ± 0.09c
Chinese cabbage	1.58 ± 0.07d	25.5 ± 1.43b	3.67 ± 0.16a	0.83 ± 0.06f	4.66 ± 0.17d	3.28 ± 0.12b
Water spinach	4.46 ± 0.20a	17.2 ± 1.15c	3.15 ± 0.08c	2.55 ± 0.10d	3.72 ± 0.14e	1.06 ± 0.02e
Garlic	3.04 ± 0.23b	30.4 ± 0.97a	3.47 ± 0.18b	1.84 ± 0.07e	17.0 ± 0.55a	6.51 ± 0.20a
Sweet potato	1.90 ± 0.06c	24.4 ± 1.50b	2.86 ± 0.09d	9.03 ± 0.27b	7.97 ± 0.25b	1.71 ± 0.04d
Kohlrabit	1.53 ± 0.06d	1.65 ± 0.62c	2.54 ± 0.08e	5.80 ± 0.30c	4.67 ± 0.10d	0.75 ± 0.02f

Values of mean concentrations in the same column followed by different small letters are significantly different at $p < 0.05$ according to Duncan's test.

limitation; hence, it is not safe to consume the two vegetables.

The concentrations of As in edible parts were in the order of garlic > Chinese cabbage > sweet potato > water spinach > lettuce > kohlrabi (Fig. 2b), far above those in a tungsten mine, southern China (Liu et al. 2010a). Compared with the contamination limitations in food set by SEPA (0.5 mg kg^{-1}) (NFHPC, 2012) and WHO/FAO (0.1 mg kg^{-1}) (2001), the vegetables exceeded 10–100 folds of the standards. It is harmful to health if long term consumption of these vegetables.

The Pb concentrations in shoots of vegetables were in the range of 3.67–5.31 mg kg^{-1}, and Chinese cabbage and kohlrabi had the highest and lowest Pb, respectively (Fig. 2c). The mean Pb levels in edible parts of the six vegetables were above the tolerance limitation of WHO/FAO (0.3 mg kg^{-1}) (2001), but lower than standard of China (9.0 mg kg^{-1}). Cadmium is chemically similar to zinc (Zn), and is easily accumulated by plants (Hladun et al. 2015; Mi et al. 2019). Lettuce shoots showed significantly high level of Cd ($p < 0.05$), followed by sweet potato kohlrabi, water spinach and garlic, and Chinese cabbage was the lowest Cd accumulator (Fig. 2d). In all, the concentrations of Pb and Cd in edible parts of various vegetable species in this study were higher than those grew in farmlands adjoining to metal mining areas in Xiangtan, China (Chen et al. 2018) and Romania (Huang et al. 2017), and cropland without mining activities reported in KP Province, Pakistan (Rehman et al. 2017), respectively.

Significant high Zn concentration was detected in garlic shoots (250 mg kg^{-1}) ($p < 0.05$), but no more than 120 mg kg^{-1} Zn was found in other vegetables, of which water spinach had lowest Zn (54.6 mg kg^{-1}) (Fig. 2e). Similarly, the highest Cu level was also found in edible parts of garlic (12.0 mg kg^{-1}), and the lowest was in kohlrabi (1.38 mg kg^{-1}) (Fig. 2f). Because both Zn and Cu were essential trace elements for higher plants and almost all living organisms, there were no limitations of Zn and Cu in food set by most of the countries and regions. However, excess exposure of the two metals can also cause toxicity to plants (e.g. above 300 mg kg^{-1} Zn) (Tang et al. 2012).

3.2. Soil contamination of heavy metal(loid)s and correlation between plants and soils

High concentrations of trace metal(loid)s in soil samples were present (Table 1), with the average being 526 mg kg^{-1} of Sb, 299 mg kg^{-1} of As, 1445 mg kg^{-1} of Pb, 24 mg kg^{-1} of Cd, 1470 mg kg^{-1} of Zn and 184 mg $kg^{-1}$of Cu. Though pollution conditions have decreased during years of equilibration under natural conditions (Romero-Freire et al. 2016), the metal(loid) levels were comparable to studies in the same areas years before (Tserenpil and Liu, 2011; Yuan and Liu, 2011). Similarly, residual pollution remains after a pyrite mine spill in Spain 15 years later, indicating the pollution incidents caused long-term contamination problems in soils (Romero-Freire et al. 2016). In recent years, Sb and its compounds are considered to be an important pollutant by the USEPA (1989) and the EU (Kabata-Pendias and Mukherjee, 2007; EFSA, 2010). Compared with Sb contents (101–5045 mg kg^{-1}) in XKS Sb mine area (He, 2007), soil Sb concentrations in this study were in the lower level. The concentrations of Cd, Pb and Zn were comparable to the values in the area around the Huludao Zinc Plant reported by Lu et al. (2010).

Soil metal(loid) levels in the study area greatly exceeded the value for the "maximum permissible concentrations of potential toxic elements (PTE-MPC)" for agricultural soils according to soil quality standards of China (SEPA, 2008) and Canada (CCME, 2007) (Table 1). In addition, metal(loid) concentrations in sampling sites were 7.67–56.5 folds of the control site (Table 1), meanwhile, high concentrations of pore-water metal were detected at 0–5 cm layers of soils, highlighting the significant impact of the accidental spill on cropland soils (Yuan et al., 2017).

Soil-to-plant transfer is a matter of concern and a key component for health risk assessment (Khan et al. 2015). Great variations in TFs were observed among each vegetable and metal(loid) (Table 2). Significant high TF values of Sb (4.46×10^{-3}), Pb (3.67×10^{-3}), Cd (16.2×10^{-2}) were found in water spinach, Chinese cabbage and lettuce, respectively ($p < 0.05$). In addition, garlic had significant high TFs of As (30.4×10^{-2}), Zn (17.0×10^{-2}) and Cu (6.51×10^{-2}) (Table 2), while sweet potato and kohlrabi had smaller TFs. As the transfer factor reflecting potential capability of plants to transfer metals from soil to edible tissues, it indicated Cd, Pb, Sb and As were easily to accumulate in edible parts of lettuce, Chinese cabbage, water spinach and garlic, respectively. In addition, significant high concentrations of water-soluble Sb, As, Pb, Cd, Zn and Cu were also measured in the 0–20 cm top layer soils (Yuan et al., 2017), indicting high plant-available metal(loid) concentrations. Although the TF values of Cu, Pb and Cd were much lower for plants compared to previous studies in some other areas in Guangxi (Liu et al. 2018), it illustrated that some heavy metals like Cd are much more easily accumulated in crops. Therefore, it would increase risks of heavy metal(loid) exposure growing these vegetable species in the wastewater affected area.

3.3. Health risks of heavy metal(loid)s from vegetables

Table 3 showed the daily intake of each metal(loid) estimated according to the average vegetable consumption for both adults and children. Significant high EDI of Cd, Pb and Sb was found in lettuce, Chinese cabbage, and water spinach ($p < 0.05$), respectively. Garlic had significant high EDI of As, Zn and Cu ($p < 0.05$), whereas sweet potato and kohlrabi had low EDI of metal(loid)s. It illustrated that eating lettuce, Chinese cabbage, water spinach and garlic had more exposure dose to Cd, Pb, Sb, As, Zn and Cu. The EDIs of Sb and As via each vegetable for residents were several times more than those in the antimony mine area of XKS (Sb 2.40 μg $(kg\text{-}d)^{-1}$ and As 5.10 μg $(kg\text{-}d)^{-1}$) (Wu et al. 2011). Compared with the non-mining area, such as secondary school students in Hong Kong (Sb 0.036 μg $(kg\text{-}d)^{-1}$) (Chung et al. 2008), EDIs of Sb in this study were thousands orders of magnitude higher. Similarly, the EDIs of Cu, Zn, Cd and Pb were also higher than other studies (Khan et al. 2008; Luo et al. 2011; Islam et al. 2014; Yuan et al. 2014; Rehman et al. 2017). Furthermore, even the lowest EDI of metal(loid) exceeded the reference dose set by USEPA (2012) (Table .3). This result was consistent with previous reports that the mean EDIs for children were markedly higher than those of adults (Khan et al. 2015; Rehman et al. 2017). In addition, the SEDI was declining with the order of Sb < Cd < Pb < Cu < As < Zn, and it

Table 3
Mean estimated daily intake (EDI) of heavy metal(loid)s through vegetable consumption (μg (kg-d)$^{-1}$) .

Vegetable	Sb		As		Pb		Cd		Zn		Cu	
	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child
Lettuce	2.83 ± 0.19e	6.02 ± 0.41e	28.5 ± 1.78c	60.4 ± 3.78c	21.7 ± 1.22e	46.0 ± 2.58e	22.4 ± 1.49a	47.5 ± 3.17a	453 ± 9.75c	963 ± 20.7c	20.0 ± 1.00c	42.6 ± 2.12c
Chinese cabbage	4.78 ± 0.22d	10.2 ± 0.47d	43.8 ± 2.46b	93.0 ± 5.21b	30.5 ± 1.35a	64.8 ± 2.87a	1.15 ± 0.08f	2.44 ± 0.17f	394 ± 14.1d	837 ± 29.9d	34.7 ± 1.25b	73.7 ± 2.65b
Water spinach	13.5 ± 0.62a	28.7 ± 1.31a	29.6 ± 1.97c	62.8 ± 4.19c	26.2 ± 0.64c	55.6 ± 1.35c	3.52 ± 0.13d	7.48 ± 0.28d	314 ± 11.4e	667 ± 24.3e	11.2 ± 0.21e	23.8 ± 0.44e
Garlic	9.20 ± 0.70b	19.5 ± 1.49b	52.2 ± 1.66a	111 ± 3.53a	28.8 ± 1.53b	61.2 ± 3.24b	2.54 ± 0.09e	5.40 ± 0.20e	1440 ± 46.2a	3059 ± 98.0a	68.8 ± 2.14a	146 ± 4.55a
Sweet potato	5.74 ± 0.18c	12.2 ± 0.39c	42.0 ± 2.58b	89.3 ± 5.48b	23.7 ± 0.76d	50.4 ± 1.62d	12.5 ± 0.37b	26.5 ± 0.79b	673 ± 20.9b	1430 ± 44.4b	18.1 ± 0.44d	38.3 ± 0.93d
Kohlrabi	4.64 ± 0.19d	9.86 ± 0.41d	28.4 ± 1.06c	60.4 ± 2.25c	21.1 ± 0.66e	44.8 ± 1.40e	8.00 ± 0.42c	17.0 ± 0.88c	395 ± 8.05d	839 ± 17.1d	7.92 ± 0.17f	16.8 ± 0.36f
Site-specific EDI	25.4	54.0	128	272	85.5	182	25.6	54.4	2231	4737	90.6	192
Reference dose [a]	0.4		0.3		3.5		1		300		4	

[a] USEPA 2012. Values of EDI in the same column followed by different small letters are significantly different at $p < 0.05$ according to Duncan's test.

ranged from 25.4 μg (kg-d)$^{-1}$ to 2231 μg (kg-d)$^{-1}$ for adult and from 54.0 μg (kg-d)$^{-1}$ to 4373 μg (kg-d)$^{-1}$ for child (Table 3). It showed greater potential health risk of Zn and As exposure occurred through vegetable consumption.

Table 4 and Table S2 (supplementary materials) illustrated the non-carcinogenic (nc) THQ for heavy metal(loid)s in each vegetable. Lettuce and water spinach had significant high THQ of Cd and Sb ($p < 0.05$) (Table 4), and the highest THQ of As was in garlic. While insignificant high THQ of Pb, Zn and Cu were present in vegetables. Furthermore, the THQ values for Cd in this study were greater than that reported by Chen et al. (2018) in Hunan Province of China, and by Rehman et al. (2017) in Parkistan. Generally, the STHQs of As and Cd in lettuce at 5% for both child and adult, as well as Sb in Chinese cabbage and water spinach for child (Table S2), were higher than the non-carcinogenic safe level of 1, indicating that there was a potential health risk to the local residents. In addition, there were no obvious non-carcinogenic risks of Cu, Zn and Pb through vegetables (Tables 4 and S2). However, even if the THQs < 1, people still pose an unacceptable risk via consumption of the vegetables due to the higher exposure in the contaminated area (Augustsson et al. 2018). For child, there was a chance of causing non-cancer risk in garlic, as STHQ of Sb > 1 at 95% (Table S2). Hence, at least 5% of the vegetable were detrimental to child. It indicated that local residents exposed to some potential health risks through the intake of As, Cd and Sb via consuming locally grown vegetables. Furthermore, child's STHQ was two folds of the adult, due to higher SEDI of heavy hmetal(loid)s. Therefore, more attention should be paid to child and potential health risk of As in vegetables.

As multiple heavy metal(loid)s in vegetable in excess of the contamination standards, therefore, it was more reasonable to use hazard index (HI) to denote non-carcinogenic health risk effects (Tables 4 and S3). Similarly, the HI values of Pb and Cd in the mining area were much higher than previous report (Rehman et al. 2017). The mean HI was in the descending order of kohlrabi < Chinese cabbage < lettuce < water spinach < sweet potato < garlic. The mean HI values for all the vegetables ranged from 50.1 to 85.0 for adult and 106 to 180 for child (Table 4), 50–180 folds of the safe level (> 1). If considered food frequency, the site-specific HI turned to the declining order: kohlrabi < water spinach < sweet potato < garlic < Chinese cabbage < lettuce (Table S2). In addition, the site-specific HI values were several to decades folds of the safe level. Therefore, non-carcinogenic health risks are likely to occur and a much greater health risk occur eating lettuce and Chinese cabbage.

Given that As and Cd have been listed as carcinogens, the carcinogenic risk were also considered. Table S4 (supplementary materials) and Fig. 3 clearly showed the cancer risk of each vegetable on both adult and child. Generally, insignificant differences of SCR of As were present, and medium values were from 0.41×10^{-3} to 1.90×10^{-3} on adult and 0.87×10^{-3} to 4.02×10^{-3} on child, respectively (Table S4). In contrast, the SCR of Cd had significant differences among the vegetables, ranging from 0.15×10^{-3} to 3.98×10^{-3} on adult and 0.32×10^{-3} to 8.45×10^{-3} on child (Table S3). Great differences also appeared for box plots of CR_n on both adult and child (Fig. 3), and lettuce had the highest cancer risk while water spinach had the lowest. However, all CR_n values at 5% were hundreds times of safety level of 5.0×10^{-5} set by ICRP (Yuan et al. 2014). Similarly, considering of the food frequency, the site-specific of CR_n values might be 1.09×10^{-2} and 2.32×10^{-2} for adult and child, respectively, hundreds times higher than the safety level. Hence, high consumption of contaminated vegetables, especially lettuce and Chinese cabbage, in these areas may increase cancer risk. Although there is no distinction for the potential cancer risk of long-term vegetables consuming on child and adult from the models (Fig. 3), as the cancer risk usually shared by the whole life of people, however, child is more vulnerable to toxic substances in reality.

Intake of heavy metal(loid)-contaminated food at elevated levels may pose a risk to the human health. Lead and Cd are listed as potential carcinogens by USEPA and EU, associated with various fatal illness such

Table 4
Non-carcinogenic health risk (THQ) of heavy metals through vegetable consumption.

THQ Vegetables	Sb		As		Pb		Cd		Zn		Cu		HI	
	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child
Lettuce	7.08e	15.0e	28.5c	60.4c	0.54e	1.15e	22.4a	47.5a	1.51c	3.21c	0.50c	1.07c	60.5d	128d
Chinese cabbage	12.0d	25.4d	43.8b	93.0b	0.76a	1.62a	1.15f	2.44f	1.31d	2.78d	0.86b	1.84b	59.9d	127d
Water spinach	33.7a	71.5a	29.6c	62.8c	0.65c	1.39c	3.52d	7.48d	1.05e	2.22e	0.23e	0.59e	68.8c	146c
Garlic	23.0b	48.8b	52.2a	111a	0.72b	1.53b	2.54e	5.40e	4.80a	10.2a	1.72a	3.65a	85.0a	180a
Sweet potato	14.3c	30.5c	42.0b	89.3b	0.59d	1.26d	12.5b	26.5b	2.25b	4.77b	0.45d	0.96d	72.1b	153b
Kohlrabi	11.6d	24.6d	28.4c	60.4c	0.53e	1.12e	8.00c	17.0c	1.32d	2.80d	0.20f	0.42f	50.1e	106e

Values of health risk in the same column followed by different small letters are significantly different at $p < 0.05$ according to Duncan's test.

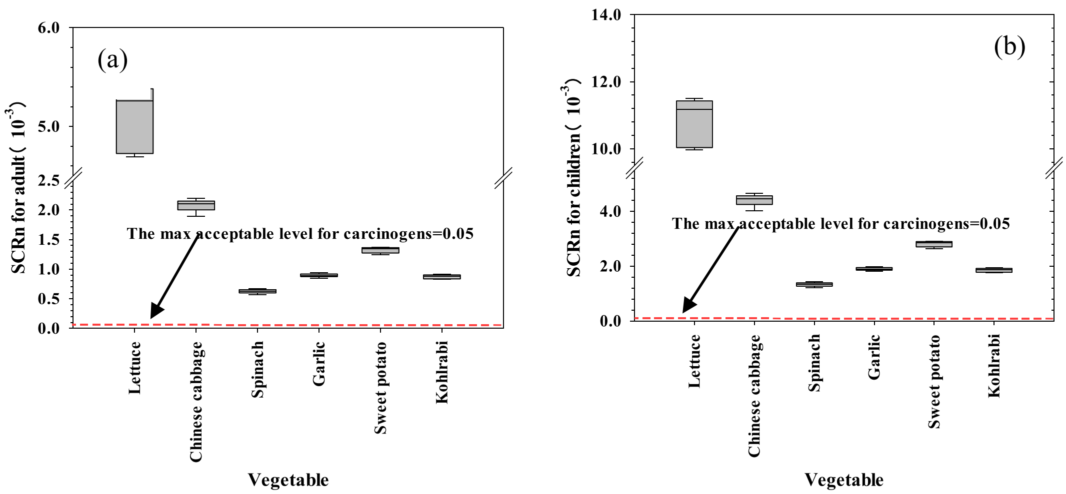

Fig. 3. Box plot of total cancer risk (CR_n) of vegetable intake based on total As and Cd concentrations on adult and child (1–14years old) in 6 different types of vegetables.

as kidney failure and diseases of bone and the nervous system (Jarup, 2003; Kabata-Pendias and Mukherjee, 2007; Garcia-Leston et al. 2010). Arsenic is known to be highly toxic to humans and animals, and can cause mutagenic, carcinogenic and teratogenic effects (Jarup, 2003; Kabata-Pendias and Mukherjee, 2007). Antimony is a cumulative poison, and also cause carcinogenic and mutagenic problems to human (Kabata-Pendias and Mukherjee, 2007; Sundar and Chakravarty, 2010). Although Zn and Cu are essential elements, they are toxicity to humans and animals at excessive concentration in food and feed plants (Kabata-Pendias and Mukherjee, 2007). In addition, heavy metal(loid)s are persistent pollutants that can be biomagnified via food chain, and even a moderate metal(loid) increase in crops may lead to a remarkable increase in exposure (Augustsson et al. 2018; Rai et al. 2019), and long-term exposure may increase the potential risk of cancers (Lu et al. 2015). Generally, the results reflected the adverse health risks of vegetables influenced by the accident. Certainly, there might be as low carcinogenic health risks to residents due to assessment systems only based on concentrations of a certain toxic element in vegetables (Khan et al. 2013; Augustsson et al. 2018). Antimony and Pb are potential carcinogens, and excess intake results in cancers, cardiovascular disease, liver disease and respiratory disease (Jarup, 2003; Kabata-Pendias and Mukherjee, 2007; Garcia-Leston et al. 2010; Sundar and Chakravarty, 2010; Feng et al. 2013). However, limited information of cancer slope factor for these elements, the cancer risks were not calculated. In addition, the adverse health risk of rice (the staple food) growing nearby should be considered, and further studies are also necessary to contain other sources of exposure, including dermal contact, dust inhalation, and ingestion of metal(loid)-contaminated soils.

Furthermore, toxicological effects of metal(loid)-contaminated food to human beings are based on various factors, such as gender, age, nutritional source, and biological species, dose, exposure route, time, frequency, as well as chemical forms of heavy metals (Khan et al. 2015; Rai et al. 2019). Therefore, more factors are required to understand the problem and risk involved in further studies. Even so, the increase in exposure is unavoidable as long as consumption of metal(loid) accumulated vegetables(Augustsson et al. 2018).

4. Conclusion

Serious pollution of heavy metal(loid)s is still present in the croplands affected by the spill of smelting wastewater several years after natural equilibration. High soluble concentrations enhanced heavy metal(loid)s accumulated in green plants. Concentrations of heavy metal(loid)s in vegetables were much higher than the safe limits of FAO/WHO and China. The result indicated that local residents were probably exposed to carcinogenic and non-carcinogenic health risks to toxic metals, especially As and Cd, via consuming homegrown vegetables. Studies also showed that child was more susceptible to heavy metal pollution than adults. Our findings revealed that a sudden pollution accident would cause long-term adverse effects to the environment safety. People should pay attention to human health through food chain, and the government should put in a bit more effort on pollution remediation and reduce the damage of pollution to human health. These results may also shed light on assessment of temporal and spatial perspectives in other country's pollution accidents.

Conflicts of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecoenv.2019.109401.

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