



## Risk assessment for potentially toxic metal(loid)s in potatoes in the indigenous zinc smelting area of northwestern Guizhou Province, China



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### ARTICLE INFO

#### Keywords:

Potentially toxic metal(loid)s  
Indigenous zinc smelting  
*Solanum tuberosum* L.  
Enrichment factor  
Bioconcentration factor  
Health risk index

### ABSTRACT

We investigated potentially toxic metal (loid)s (arsenic, As; cadmium, Cd; chromium, Cr; copper, Cu; mercury, Hg; lead, Pb; selenium, Se; and zinc, Zn) in agricultural samples (i.e., *Solanum tuberosum* L. tubers (potatoes) and their planting media) in the indigenous zinc smelting area of northwestern Guizhou Province, China. Based on the pollution index values for As, Cd, Pb and Zn, the order of the samples was as follow: slag > planting soil with slag > planting soil without slag, and the order of the samples in terms of the bioconcentration factor was the opposite. Cr, Cu and Hg were present in the planting soil with and without slag at slight pollution levels, and the other potentially toxic metal (loid)s had different degrees of contamination. Additionally, the potentially toxic metal (loid) contents in potato were under their limit values except for Cd (all samples) and Pb and Se (some samples). All bioconcentration factors for potatoes were below 0.5, and no health risk index value for potatoes was higher than 0.1. Therefore, although no significant health risk associated with potentially toxic metal (loid)s via consuming potato exists for either adult men or women in the research area, the Cd concentration in this crop should be monitored.

### 1. Introduction

Potentially toxic metal (loid)s include the 11 most environmentally important metal (loid)s, i.e., arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), mercury (Hg), lead (Pb), manganese (Mn), nickel (Ni), selenium (Se) and zinc (Zn), and other less known but environmentally important elements (Alloway, 2013). We selected and analyzed eight potentially toxic metal (loid)s – As, Cd, Cr, Cu, Hg, Pb, Se and Zn – according to the potentially toxic limits for these eight metal (loid)s in cereals, legumes, tubers and their products (MAPPC, 2005), because these eight metal (loid)s are used in industry and are generally toxic (Smith and Scott, 2005).

Although indigenous zinc smelting has been banned by local governments (in 2006 in the northwestern region of Guizhou Province and in 2003 in the north of France (Batonneau et al., 2004), the environmental impacts of this process persist. The slag produced by indigenous zinc smelting has been stored in the surrounding surface soil of the smelter sites without treatment, which has resulted in serious contamination and environmental risk (Peng et al., 2018). Furthermore, this slag contains high concentrations of potentially toxic metal (loid)s that are released over long periods of time (Wu et al., 2002). Although

most of the potentially toxic metal (loid)s in this slag are generally dominated by polymetallic or other phases (e.g., sulfide-rich phases) (Ettler et al., 2003; Scokart et al., 1983; Sobanska et al., 2016), they can be easily transported due to long-term natural weathering (Deng et al., 2015; Ma et al., 2015; Sobanska et al., 2016; Tyszkla et al., 2014) or other processes occurring in acidic (low-pH) environments (Scokart et al., 1983; Sobanska et al., 2016; Yang et al., 2006).

Additionally, potentially toxic metal (loid) contamination, especially in food, is a very important issue for plants, animals and human beings. Potentially toxic metal (loid) pollution is a global problem because it could influence human health via respiration, food, and drinking water (Siegel, 2002). Potentially toxic metal (loid)s play a vital part role in the health of plants, animals and human beings, either directly or indirectly (Peng et al., 2017). Chronic intake of potentially toxic metal (loid)s has damaging effects on human beings and other animals (Zheng et al., 2007). Food is a dominant source of potentially toxic metal (loid) exposure (Ferrante et al., 2018). The accumulation of heavy metals in crops may create a potential public health risk (Cherfi et al., 2014; Gebrekidan et al., 2013; Nagajyoti et al., 2010; Pinto et al., 2015; Skalnaya et al., 2018; Zhang et al., 2018), because they are toxic to humans and plant tissues (Khan et al., 2015). Moreover, conditions in

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<https://doi.org/10.1016/j.fct.2018.07.026>

Received 18 February 2018; Received in revised form 9 July 2018; Accepted 13 July 2018

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which the concentrations of these potentially toxic metal (loid)s are too high or are totally lacking can lead to adverse health effects (Erdman Jr et al., 2012; Ferrante et al., 2017a, 2017b; Fraga, 2005; Jomova and Valko, 2011; Kakkar and Jaffery, 2005; Satarug, 2018; Satarug et al., 2017; Tinkov et al., 2018; Zhang et al., 2018). Therefore, local residents might have elevated health risks from the ingestion of potentially toxic metal (loid)s via food crops grown in the indigenous zinc smelting area.

The health risks associated with potato consumption with respect to potentially toxic metal (loid)s are a very important issue. Potatoes (*Solanum tuberosum* L.), which belong to the *Solanaceae* family, are perennial herbs with edible tubers. In addition, the potato has a high nutritional value, such as a high protein content (containing 18 kinds of essential amino acids, including various amino acids that the human body cannot synthesize), abundant vitamins (including vitamin C and a variety of other vitamins that are useful for the human body), abundant dietary fiber and little fat. *Solanum tuberosum* L. is also the fourth largest food crop in the world; it plays an irreplaceable role in ensuring food security and achieving the Millennium Development Goals (Xie, 2012). According to 2016 data from the Food and Agriculture Organization (FAO) (<http://faostat.fao.org/>), the worldwide planting acreage and yield of *Solanum tuberosum* L. are approximately  $1924.65 \times 10^4$  hm<sup>2</sup> and  $3.77 \times 10^8$  t, respectively. In China, the *Solanum tuberosum* L. planting acreage is approximately  $581.51 \times 10^4$  hm<sup>2</sup> (accounting for 30.21% of the global planted area), and fresh potato production is approximately  $0.99 \times 10^8$  t (26.25% the global annual production); both the planting acreage and yield of *Solanum tuberosum* L. in China ranked first in the world. The Chinese Ministry of Agriculture issued “guidance on promoting the development of the potato industry” on February 23, 2016. The potato was established as a staple food product for industrial development. Meanwhile, it is also suggested that by 2020, the potato planting area will have expanded to more than 100 million acres. The proportion of varieties suitable for staple food processing will reach 30%, and the consumption of staple food will account for 30% of the total potato consumption. Additionally, the northwestern region of Guizhou Province is also an important planting base for *Solanum tuberosum* L. in Guizhou Province.

Moreover, *Solanum tuberosum* L. and *Zea mays* L. are two common and widely grown crops in the area surrounding the indigenous zinc smelting slag in the northwestern region of Guizhou Province. And *Solanum tuberosum* L. is usually intercropped with *Zea mays* L. In this area, some slag is commonly present in the soil in which the crops (i.e. *Solanum tuberosum* L. and *Zea mays* L.) are grown. Thus, the food safety of potatoes represents an important issue in relation to people's health and needs to be solved, especially in areas contaminated with potentially toxic metal (loid)s (i.e., the indigenous zinc smelting area in the northwestern region of Guizhou Province). Although some researchers have studied the presence of potentially toxic metal (loid)s in potato and vegetables (i.e., Cd in *Solanum tuberosum* L. (Fu et al., 2014) and Cd, Pb and Zn in vegetables (Yang et al., 2011b) in the indigenous zinc smelting area; Cd of potato in Weining County (Zhang et al., 2017); 12 elements (Briki et al., 2015) and 10 elements (Shao et al., 2018) in vegetables in Hezhang County), few have focused on evaluating the potentially toxic metal (loid)s present in potato grown in different planting media, especially indigenous zinc smelting slag. Therefore, in this study, the distribution analysis and risk assessment of eight potentially toxic metal (loid)s – As, Cd, Cr, Cu, Hg, Pb, Se and Zn – in *Solanum tuberosum* L. tubers (potatoes) grown in different planting environments were carried out in the indigenous zinc smelting area in the northwestern region of Guizhou Province, China. The aim was to better understand the contamination of the cultivated area and the impact on crops and to develop some recommendations for improving crops in the research area.

## 2. Materials and methods

### 2.1. Research area

The research area in this study is mainly in Weining and Hezhang Counties, northwestern Guizhou Province, where concentrated indigenous zinc smelting occurred. The area has elevations ranging from 1185 to 2901 m, and an average elevation of more than 2000 m (CCCBBGP, 1995). The region features a humid subtropical climate: the annual average sunshine ranges from 1380.5 to 1769.8 h, the temperature ranges from 10.5 to 13.4°C, the average annual rainfall ranges from 849.2 to 934.8 mm, and the frost-free period lasts for more than 209 days (CCCBBGP, 1995). In addition, the research area exhibits clear plateau climatic characteristics, such as small annual changes in air temperature and large diurnal changes in air temperature. The large diurnal change in air temperature is conducive to the accumulation of dry crop material. In Weining County especially, there covers more than 80% of the area at elevations above 2000 m, which is suitable for planting *Solanum tuberosum* L. and sweet beet crops. Therefore, Weining County is an important planting area for *Solanum tuberosum* L. and sweet beets. Moreover, there is a long history of planting *Solanum tuberosum* L. in Weining County. As early as April 2008, Weining County was awarded the title of “potato town of South China” by the Potato Specialized Committee of China's Food Industry Association.

### 2.2. Collecting samples

In August 2015, we collected a total of 38 samples of potatoes and their planting media (i.e., indigenous zinc smelting slag, planting soil with slag and planting soil without slag around the slag pile; samples were collected from a depth range from 0 to 20 cm) from 19 different sampling sites in the indigenous zinc smelting area (Fig. 1). These sampling sites (i.e., Bojigou: BJG, Xingfayingpanzai: XFYPZ, Xingfa: XF, Jiaomeiba: JMB, Yingpanzai: YPZ, Caoziping: CZP, Huangjiagai: HJZ, Lianmincun: LMC, Lushanxingzhuangcun: LSXZC, Liangshuigou: LSG, Fuweijiaohuachang: FWJHC, two sampling sites in Leijiaping: LJP and Yancangliangshuijing: YCLSJ, and three sampling sites in Chayuan: CY) were located near some typical piles of indigenous zinc smelting slag and its surrounding soils planted with *Solanum tuberosum* L. The planting media included 9 samples of indigenous zinc smelting slag, 4 samples of planting soil with slag, and 6 samples of planting soil without slag around the slag pile, as shown in Table 1.

### 2.3. Sample analyses

The methods and preparation of the sample analyses followed those in the references (Peng et al., 2018, 2017).

#### 2.3.1. Analysis of the planting media samples

The samples of the planting media (slag, planting soil with slag and planting soil without slag from locations around the slag pile; each sample was approximately 1 kg) were halved by applying the quartering method after removing foreign substances. One-half of each sample was dried at 30°C to a constant weight in a thermostatic air-blower-driven drying closet and then sieved with a 10-mesh nylon sieve. The pH of each dry sieved sample (10.00 g of sample mixed with 25 ml deionized water) was determined by a pen pH meter (SX620 type, Instrument Factory of Shanghai Sanxin, Shanghai, China). In addition, we sent 100 g of each dry samples to an accredited laboratory (ALS Minerals – ALS Chemex (Guangzhou) Co. Ltd.) to determine the concentrations of potentially toxic metal (loid) (As, Cd, Cr, Cu, Hg, Pb and Zn) (Peng et al., 2018, 2017). The simple analysis procedure for the planting media samples was as follows (Peng et al., 2018).

One hundred grams of each of the dry samples was gently disaggregated with a rubber hammer and sieved through an 80-mesh sieve (0.18 mm) to remove other foreign substances (e.g., gravel, iron

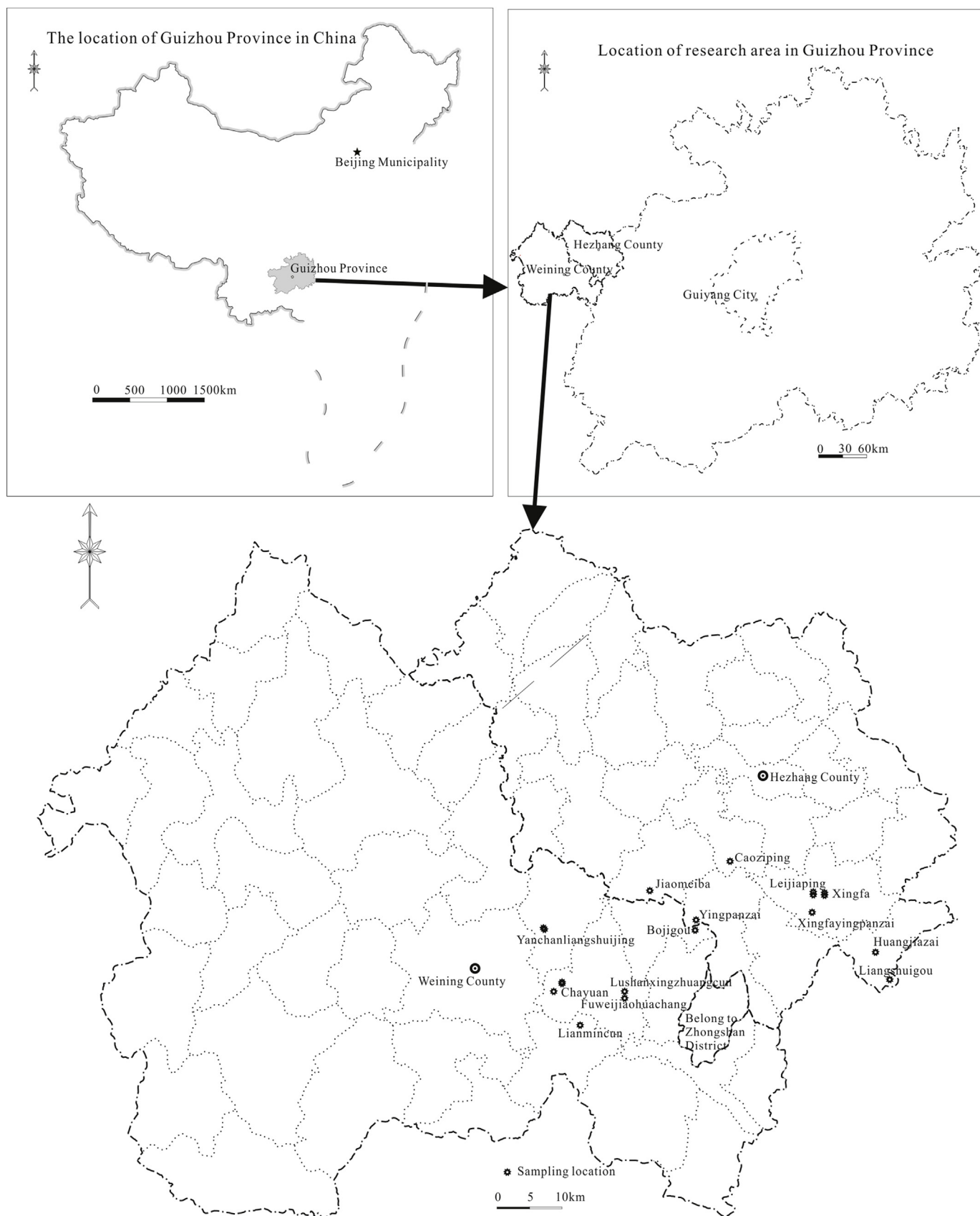


Fig. 1. Sampling locations in the research area.

**Table 1**  
Potentially toxic metal (loid) concentrations and pH values of the potato planting media in the indigenous zinc smelting area.

Sample type	Sample	As	Cd	Cr	Cu	Hg	Pb	Se	Zn	Al	pH
Indigenous zinc smelting slag	JMBTR	338.0	46.00	96	354	0.351	8140	4.7	10,300	6.91	8.02
	CZPTR	1320.0	35.10	83	648	2.240	9830	8.6	15,400	6.14	8.02
	JZLMCTR	304.0	17.90	73	2690	0.019	1680	3.2	6690	6.54	8.34
	CPTR	84.2	20.80	111	111	0.297	1840	2.9	12,150	6.49	7.42
	YCLSJTR1	814.0	70.70	75	123	0.265	20,100	8.5	26,900	5.37	7.72
	CYTR2	229.0	66.30	124	207	0.186	6780	3.8	14,550	6.19	7.96
	CYTR4	209.0	16.05	75	191	0.207	5020	4.3	17,150	5.32	8.10
	FWJHZ	746.0	193.50	89	4580	0.081	8560	7.9	13,900	4.91	7.26
	XFTR2	293.0	28.90	233	219	0.817	1870	3.4	22,800	9.24	6.72
	Average	481.91	55.03	106.56	1013.67	0.50	7091.11	5.26	15,537.78	6.35	7.73
	Planting soil with slag	LJPTR2	114.5	8.08	114	303	0.170	374	1.3	12,550	8.33
CYTR1		36.3	8.73	203	128	0.131	955	1.6	2430	8.63	7.55
YCLSJTR2		64.0	21.00	36	22	0.160	1480	1.0	3830	3.01	6.61
BJGTR		38.8	3.84	84	36	0.107	185	1.1	1120	6.48	4.29
Average		63.40	10.41	109.25	122.25	0.14	748.50	1.25	4982.50	6.61	6.21
Planting soil without slag	LJPTR1	12.0	1.16	126	187	0.188	62	1.1	249	10.70	5.60
	LSXZCTR	12.0	0.88	254	110	0.114	28	0.5	153	10.05	4.74
	HJZTR	14.2	1.48	187	110	0.084	58	0.9	270	8.03	4.81
	LSGTR	7.2	1.11	91	161	0.079	38	0.5	193	10.40	4.52
	YPZTR	20.2	6.50	89	41	0.130	105	0.9	309	5.99	4.64
	XFTR3-1	18.8	1.08	214	145	0.137	86	0.9	386	11.70	4.66
Average	14.07	2.04	160.17	125.67	0.12	62.83	0.80	260.00	9.48	4.83	
Crustal average		1.8	0.2	100	55	0.08	12.5	0.05	70		8.23
The Class II level of upland soil environmental quality standard in China (6.5 < soil pH < 7.5)		30	0.3	200	100	0.5	300		250		

Note: The pH is constant, the unit of the element Al is percent, and units of other elements are mg/kg. The crustal average is the average abundance of chemical elements in the continental crust (Taylor, 1964). The Class II level of upland soil environmental quality standard in China refers to the soil quality value of grade two (CEPA and CTSA, 1995).

manganese nodules, and plant residue), and these sieved samples were then separated into two parts for analysis and for storage.

Two test samples (0.25 g and 0.50 g) were weighed from each prepared planting medium sample. The first sample (0.25 g) was digested with perchloric, nitric and hydrofluoric acids; the residue was leached with dilute hydrochloric acid and diluted to volume. The final solution was then analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, America, Varian VISTA) and inductively coupled plasma mass spectrometry (ICP-MS, America, Agilent 7700x) (Peng et al., 2018). The other sample (0.50 g) was digested with aqua regia in a graphite heating block. After cooling, the resulting solution was diluted to volume with deionized water, mixed and analyzed by ICP-AES followed by ICP-MS for the remaining suite of elements (Peng et al., 2018). According to the actual characteristics of the sample, the digestion effect and interelement spectral interferences, the comprehensive value was the final test result.

### 2.3.2. Analysis of the potato sample

Three potatoes of similar sizes were selected from each potato sample. The fresh potatoes were washed with high-pressure tap water until all soil and other foreign substances were removed. In addition, the washed potatoes were peeled with a peeling knife to remove approximately 2 mm of the epidermis of the potato. The peeled potatoes were washed with high-pressure tap water and rinsed with deionized water 2 or 3 times. After cleaning, the potatoes were cut into approximately 1-cm cubes. The cubes of potatoes were dried at 50 °C for two hours and then at 30 °C to a constant weight in a thermostatic air-blower-driven drying closet. The dry samples were then ground in an agate mortar and sieved in a nylon sieve ( $\leq 149 \mu\text{m}$ ). We sent 5 g of each of the sieved samples to an accredited laboratory (ALS Minerals – ALS Chemex (Guangzhou) Co. Ltd.) for determination of the potentially toxic metal (loid) concentrations. The simple analysis procedure for potato samples was as follows (Peng et al., 2018).

Each prepared dry sample (1.0 g) was cold digested for approximately 8 h in nitric acid and then heated for three hours in a graphite heating block. The samples were subsequently cooled and brought up to

volume with HCl (Peng et al., 2018). The resulting solution was mixed thoroughly and analyzed by ICP-AES (America, Varian VISTA) and ICP-MS (America, Agilent 7900) (Peng et al., 2018). According to the actual characteristics of the sample, the digestion effect and interelement spectral interferences, the comprehensive value was the final test result.

### 2.4. Data statistics and analyses

All analytical data were analyzed using Excel 2003 and IBM SPSS 22 Statistics Version 22 for Windows. Additionally, the data were tested for a normal distribution by the Shapiro-Wilk method to choose the proper statistical tools (Peng et al., 2018). The level of  $P < 0.05$  for several variables was a significant difference, and thus, nonparametric tests (of one-sample Kolmogorov-Smirnov tests) were used. Moreover, Spearman correlation analyses do not require the assumption that the relationship between the variables is linear (de Almeida Duarte et al., 2017; Ofungwu, 2014; Peng et al., 2018). Correlations among the potentially toxic metal (loid)s in the potatoes and the planting media were calculated by the Spearman test using the software SPSS at significance levels of  $P \leq 0.05$  and  $P \leq 0.01$ .

#### 2.4.1. Pollution index

The pollution index ( $PI$ ) can determine the main pollution material and the degree of harm (Ye and Luan, 1994). The  $PI$  is generally expressed as the ratio of the measured element content in the soil to the standard value of the element as follows (Hu et al., 2013; Li et al., 2006; Wu et al., 2015; Yang et al., 2011c):

$$PI = \frac{C_{PEM}}{C_0}$$

where  $PI$ ,  $C_{PEM}$ , and  $C_0$  represent the pollution index, the potentially toxic metal (loid) content in planting media and the standard value of the element, respectively. A  $PI$  value greater than 1 indicates the soil sample is polluted, while a  $PI$  value less than 1 suggests the soil sample is unpolluted (Li et al., 2006). A  $PI$  value that is greater than 1 but not greater than 3 suggests that the soil is slightly polluted, a  $PI$  value greater than 3 but not greater than 5 suggests that the soil is moderately



polluted, and a *PI* value greater than 5 suggests that the soil is seriously polluted (Wu et al., 2015).

#### 2.4.2. Enrichment factor

The enrichment factor (*EF*) expresses the relative abundance of an element, and it is a good tool for differentiating the source of a chemical element, i.e., whether the source is anthropogenic or natural (Peng et al., 2017). Rahn (1971) presents a useful way to determine whether a particular element was found in greater abundance than what might be expected from crustal sources, introducing the concept of “enrichment factors”. The *EF* is used to distinguish between anthropogenic and naturally occurring sources for trace element concentrations in air (Bilos et al., 2001) and heavy metals in sediments and soil (Chen et al., 2007; Oliva and Espinosa, 2007). The reference element mainly originates from the soil parent material and undergoes little contamination by anthropogenic activities (Wu et al., 2015). Elements that are commonly considered references for crustal material include Al, Sc, and Zr. Many researchers have used Al as the reference element to calculate the *EF*s for sediment, atmosphere and soil samples (Chen et al., 2007, 2014; 2009; Duce et al., 1975; Khorasanipour and Aftabi, 2011; Peng et al., 2017; Viers et al., 2009; Zhang et al., 1994; Zoller et al., 1974). This approach is used because the element Al is mainly derived from natural sources and it can cancel any dilution effect caused by natural composites such as carbonate, quartz, or organic matter (Chen et al., 2014, 2009). In this study, Al is considered the crustal material reference element. According to Rahn (1971) and Lee et al. (1994), the *EF* is defined as follows:

$$EF = \frac{\left(\frac{Me}{Al}\right)_{soil}}{\left(\frac{Me}{Al}\right)_{crust}}$$

Here,  $(Me/Al)$  and  $(Me/Al)$  refer to the soil and mean crustal concentration ratios (Taylor, 1964), respectively, of a metal and Al. According to Sutherland (2000) and Chen et al. (2007),  $EF < 1$ ,  $1 \leq EF < 3$ ,  $3 \leq EF < 5$ ,  $5 \leq EF < 10$ ,  $10 \leq EF < 25$ ,  $25 \leq EF < 50$  and  $EF \geq 50$  correspond to no enrichment, minor enrichment, moderate enrichment, moderately severe enrichment, severe enrichment, very severe enrichment, and extremely severe enrichment, respectively. Similarly, these value ranges also respectively correspond to no pollution, minor pollution, moderate pollution, moderate to severe pollution, severe pollution, very severe pollution and extremely severe pollution (Peng et al., 2017).

#### 2.4.3. Bioconcentration factor

The bioconcentration factor (*BCF*) represents the ratio of the element concentration in the plant to that in the growing soil (Yoon et al., 2006; Zhang et al., 2012), and it is measured by the abundance of the chemical elements in the plant (Peng et al., 2017). To measure the effectiveness of a plant's ability to concentrate a metal (loid) in its biomass, the *BCF* is defined as the ratio of the metal (loid) concentration in the plant to that in the soil (Fayiga et al., 2004). In our study, it is calculated as follows:

$$BCF = \frac{C_p}{C_{PEM}}$$

where *BCF* is the bioconcentration factor of the potentially toxic metal (loid) in a potato,  $C_p$  is the potentially toxic metal (loid) concentration in the potato, and  $C_{PEM}$  is the element concentration in the planting medium of the potato.

#### 2.4.4. Health risk index

Oral intake is a very important pathway by which potentially toxic metal (loid)s enter the human body. To calculate the levels of human exposure to potentially toxic metal (loid)s from potatoes, the average daily intake (*ADI*) and health risk index (*HRI*) were measured in this

study. According to some references (HC, 2012; Hough et al., 2004; Jan et al., 2010; Khan et al., 2008, 2010, 2017; Li et al., 2014; USEPA, 1989, 1992, 2003), the *ADI* equation by a given route is as follows:

$$ADI = \frac{C_p \times C_f \times Ir \times Ef \times Ed}{Bw \times At}$$

where *ADI* represents daily intake of potentially toxic metal (loid)s (mg/kg-day);  $C_p$  represents the potentially toxic metal (loid) concentrations in a potato (mg/kg);  $C_f$  represents the conversion factor (0.085) for conversion of fresh to dry weight vegetables (Jan et al., 2010; Rattan et al., 2005; Rehman et al., 2017); *Ir* represents the ingestion rate (g/day), according to the maximum consumption recommended in “Dietary Guidelines for Chinese Residents (2016)” (CNS, 2016), where the average intake rate of potatoes in this study is 0.100 kg/day; *Ef* represents the exposure frequency (365 days/year), *Ed* represents the exposure duration (70 years); *Bw* represents the body weight (kg), where the body weights for adult men and women are assumed to be 66.2 kg and 57.3 kg, respectively (DPCBNHFPC, 2015); and *At* represents the average time (70 years = 25,550 days).

To estimate the chronic health risk, the *HRI* for potentially toxic metal (loid)s through contaminated food-crop consumption was determined using the following (Jan et al., 2010; Khan et al., 2008; Rehman et al., 2017):

$$HRI = \frac{ADI}{Rfd}$$

Here, *HRI*, *ADI*, and *Rfd* represent the human health risk index, daily intake of potentially toxic metal (loid)s, and reference dose of potentially toxic metal (loid)s, respectively. According to a database (USEPA, 2017), the oral toxicity reference dose values (*Rfd*) for As, Cd, Cr(VI), Cu, Hg, Se and Zn are 0.0003, 0.001, 0.003, 0.04, 0.0003, 0.005 and 0.3 mg/kg/day, respectively, and that for Pb is 0.0035 mg/kg/day (Hough et al., 2004). The *Rfd* of As was set to that of inorganic As, and the *Rfd* of Cd was set to that of Cd (diet). The *Rfd* of Cr was set to the value for Cr(VI) due to the fact that Cr(VI) is more harmful to human health than Cr(III) at the same exposure concentration. The *Rfd* of Hg was set to the value for inorganic Hg in this research, because inorganic Hg species are predominant in most Hg-enriched plants, except for rice, in Hg mining areas (Feng and Qiu, 2008; Horvat et al., 2003; Qiu et al., 2008, 2006).

### 3. Results and analyses

#### 3.1. Potentially toxic metal(loid) contents in planting media

The concentrations of the potentially toxic metal (loid)s As, Cd, Pb, Se and Zn are obviously affected by the indigenous zinc smelting slag in the research area, especially those of Pb, Zn and Cd. In addition, the slag is slightly acidic or neutral, the planting soil with slag is neutral or slightly acidic, and the planting soil without slag is strongly acidic. As shown in Table 1, the potentially toxic metal (loid) contents of Pb and Zn are more than 1000 mg/kg and are higher than those of the other potentially toxic metal (loid)s. The Zn content is especially high, and the majority of samples exhibit concentrations of more than 10,000 mg/kg. These elements are followed by Cu, As, Cr, and Cd, with contents between 10 mg/kg and 1000 mg/kg. The Se and Hg contents are below 10 mg/kg and are lower than those of other elements. Additionally, the As, Cd, Cu, Pb, Se and Zn contents of the planting soil without slag around the slag pile are all lower than those of the indigenous zinc smelting slag or planting soil with slag, especially Cd, Pb and Zn. Furthermore, some potentially toxic metal (loid) contents are obviously different in the planting soil with slag; this feature might be caused by planting soil with different quantities of slag. The average contents of As, Cd, Pb, Se and Zn in the planting soil around the slag pile are lower than their contents in the slag and the planting soil with slag, especially Cd, Pb and Zn. Moreover, the slag pH is high and ranges from 6.72 to

**Table 2**  
Concentrations of potentially toxic metal (loid)s in potatoes in the indigenous zinc smelting area (mg/kg).

Planting media	Sample	As	Cd	Cr	Cu	Hg	Pb	Se	Zn	
Indigenous zinc smelting slag	JMBTD	0.022	0.254	0.14	8.34	<b>0.001</b>	0.377	0.27	37.4	
	CZPTD	0.100	0.139	0.18	7.09	0.002	0.498	0.45	25.0	
	JZLMCTD	0.136	0.160	0.07	6.02	<b>0.001</b>	0.045	0.43	25.1	
	CPTD	0.068	0.238	0.07	2.47	0.002	0.075	0.04	20.7	
	YCLSJTD1	0.147	0.207	<b>0.05</b>	1.95	<b>0.001</b>	0.417	0.03	25.8	
	CYTD2	0.124	0.455	<b>0.05</b>	4.52	<b>0.001</b>	0.315	0.08	21.8	
	CYTD4	0.109	0.130	0.06	2.13	<b>0.001</b>	0.199	0.25	12.0	
	FWJHTD	0.099	0.879	0.06	5.04	<b>0.001</b>	0.199	0.18	16.4	
	XFTD1	0.127	0.211	0.29	3.42	0.001	0.036	<b>0.02</b>	27.1	
	Minimum	0.022	0.130	0.05	1.95	0.001	0.036	0.02	12.0	
	Maximum	0.147	0.879	0.29	8.34	0.002	0.498	0.45	37.4	
	Average	0.104	0.297	0.11	4.55	0.001	0.240	0.19	23.48	
	Planting soil with slag	LJPTD2	0.045	0.109	<b>0.05</b>	5.14	0.001	0.023	0.02	33.6
		CYTD1	0.108	0.571	<b>0.05</b>	1.91	<b>0.001</b>	0.113	<b>0.02</b>	23.2
YCLSJTD2		0.139	0.330	<b>0.05</b>	4.91	0.001	0.064	0.04	21.0	
BJGTD		0.059	0.340	0.05	1.34	<b>0.001</b>	0.026	<b>0.02</b>	30.4	
Minimum		0.045	0.109	0.05	1.34	0.001	0.023	0.02	21.0	
Maximum		0.139	0.571	0.05	5.14	0.001	0.113	0.04	33.6	
Average		0.088	0.338	0.05	3.33	0.001	0.057	0.03	27.05	
Planting soil without slag		LJPTD1	0.013	0.329	0.20	4.68	<b>0.001</b>	0.114	0.03	16.3
		LSXZCTD	0.114	0.543	0.10	6.22	0.001	1.230	<b>0.02</b>	27.2
		HJZTD	0.111	0.185	<b>0.05</b>	4.18	<b>0.001</b>	0.019	<b>0.02</b>	10.9
	LSGTD	0.056	0.323	0.05	5.20	<b>0.001</b>	0.025	0.04	23.7	
	YPZTD	0.101	0.426	<b>0.05</b>	2.19	<b>0.001</b>	0.034	<b>0.02</b>	23.9	
	XFTD2	0.140	0.209	0.05	6.35	0.002	0.229	0.02	22.2	
	Minimum	0.013	0.185	0.05	2.19	0.001	0.019	0.02	10.9	
	Maximum	0.140	0.543	0.20	6.35	0.002	1.230	0.04	27.2	
	Average	0.089	0.336	0.08	4.80	0.001	0.275	0.03	20.70	
	Minimum	0.013	0.109	<b>0.05</b>	1.34	<b>0.001</b>	0.019	<b>0.02</b>	10.9	
Maximum	0.147	0.879	0.29	8.34	0.002	1.230	0.45	37.4		
Average	0.096	0.318	0.09	4.37	0.001	0.213	0.11	23.35		
NY861-2004	0.5	0.05	1	20	0.02	1	0.3	50		

Note: A bold number means the element concentration of the sample is below the lowest detection limit, and we assume that the element content is equal to the lowest detection limit in the calculations and analysis in this article, the same below. The row for NY861-2004 is derived from the literature (MAPP, 2005).

8.34. The pH of the planting soil without slag around the slag pile is low and ranges from 4.52 to 5.60. In addition, the pH of the planting soil with slag is highly variable (ranging from 4.29 to 7.55).

3.2. Potentially toxic metal(loid) contents of potatoes

There is little difference in the potentially toxic metal (loid) contents of potatoes planted in different planting media in the indigenous zinc smelting area. As shown in Table 2, the average contents of the potentially toxic metal (loid)s As, Cd, Cr, Cu, Hg, Pb, Se and Zn in potatoes are respectively 0.096 mg/kg (ranging from 0.013 to 0.147 mg/kg), 0.318 mg/kg (0.109–0.879 mg/kg), 0.09 mg/kg (0.05–0.29 mg/kg), 4.37 mg/kg (1.34–8.34 mg/kg), 0.001 mg/kg (0.001–0.002 mg/kg), 0.213 mg/kg (0.019–1.230 mg/kg), 0.11 mg/kg (0.02–0.45 mg/kg) and 23.4 mg/kg (10.9–37.4 mg/kg) in the research area. In addition, according to the averages and ranges of the potentially toxic metal (loid)s, the contents of As, Cd, Cu, Hg and Zn are similar among the potatoes planted in the different planting media (i.e., indigenous zinc smelting slag, planting soil with slag and planting soil without slag surrounding the slag pile).

3.3. Pollution index

Cd contamination is obvious in the planting media in the research area, especially Cd pollution in the slag. The PI values for As, Cd, Cu, Pb, and Zn in the indigenous zinc smelting slag and planting soil with slag are larger than 1, except for Cu and Pb in a few samples. The PI values for Cd, Cu and Zn in the planting soil without slag around the slag pile are also greater than 1, except for Cu and Zn in a few samples. Furthermore, the PI values for the remaining elements are less than 1 in the indigenous zinc smelting area (Fig. 2). Moreover, in the terms of the PI values for As, Cd, Pb and Zn, the potato planting media are usually in

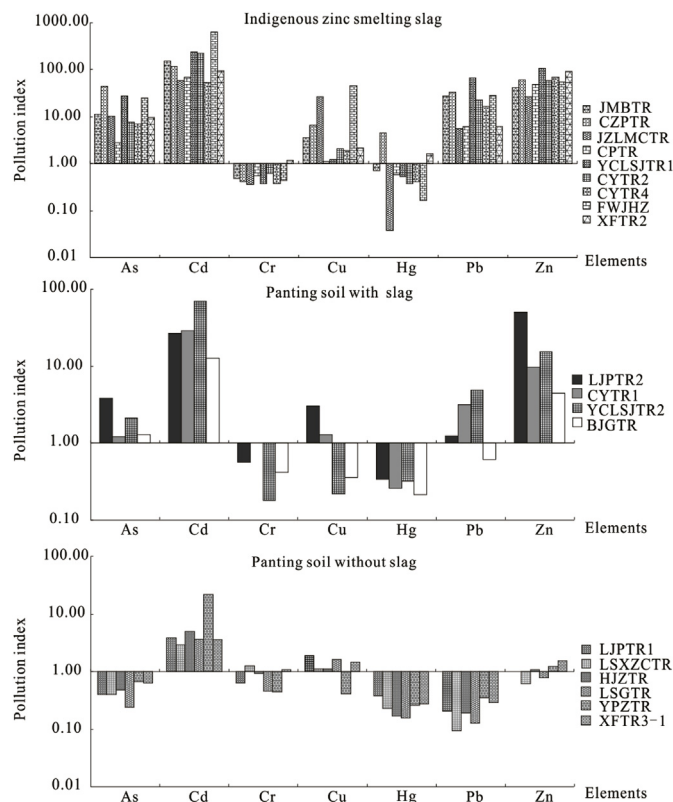


Fig. 2. PI values for potentially toxic metal (loid)s in the planting media in the indigenous zinc smelting area.

**Table 3**  
EFs of potentially toxic metal (loid)s in the planting media in the indigenous zinc smelting area.

Sample type	Sample	As	Cd	Cr	Cu	Hg	Pb	Se	Zn
Indigenous zinc smelting slag	JMBTR	223.65	273.94	1.14	7.67	5.23	775.60	111.96	175.25
	CZPTR	982.95	235.24	1.11	15.79	37.53	1054.08	230.55	294.89
	JZLMCTR	212.53	112.63	0.92	61.55	0.30	169.13	80.54	120.27
	CPTR	59.32	131.88	1.41	2.56	4.71	186.67	73.55	220.11
	YCLSJTR1	693.07	541.77	1.15	3.43	5.08	2464.40	260.54	588.95
	CYTR2	169.15	440.75	1.65	5.00	3.09	721.16	101.05	276.36
	CYTR4	179.62	124.15	1.16	5.37	4.00	621.27	133.04	379.01
	FWJHZ	694.68	1621.70	1.49	139.58	1.70	1147.84	264.84	332.84
	XFTR2	144.98	128.71	2.08	3.55	9.10	133.25	60.57	290.11
	Average	373.33	401.19	1.35	27.17	7.86	808.16	146.29	297.53
	Planting soil with slag	LJPTR2	62.85	39.92	1.13	5.44	2.10	29.56	25.69
CYTR1		19.23	41.63	1.94	2.22	1.56	72.86	30.52	33.11
YCLSJTR2		97.22	287.09	0.98	1.09	5.47	323.73	54.68	149.60
BJGTR		27.38	24.39	1.07	0.83	1.70	18.80	27.94	20.32
Average		51.67	98.26	1.28	2.40	2.71	111.24	34.71	95.04
Planting soil without slag		LJPTR1	5.13	4.46	0.97	2.62	1.81	3.82	16.92
	LSXZCTR	5.46	3.60	2.08	1.64	1.17	1.83	8.19	1.79
	HJZTR	8.09	7.58	1.92	2.05	1.08	4.76	18.45	3.95
	LSGTR	3.17	4.39	0.72	2.32	0.78	2.41	7.91	2.18
	YPZTR	15.42	44.65	1.22	1.02	2.23	11.54	24.73	6.07
	XFTR3-1	7.35	3.80	1.51	1.85	1.20	4.84	12.66	3.88
	Average	7.43	11.42	1.40	1.92	1.38	4.87	14.81	3.43

the order of the slag > planting soil with slag > planting soil without slag around the slag pile.

### 3.4. Enrichment factor

In the planting soil with and without slag in the research area, the As, Cd, Pb, Se and Zn concentrations correspond to varying degrees of pollution, whereas most of Cr, Cu and Hg concentrations correspond to slight pollution. However, in the slag, the As, Cd, Pb, Se and Zn concentrations correspond to extreme pollution, and the Cr, Cu and Hg concentrations correspond to varying degrees of pollution. As presented in Table 3, in terms of the average EFs of As, Cd, Cu, Hg, Pb, Se and Zn, the planting media are usually in the order of slag > planting soil with slag > planting soil without slag around the slag pile. In the indigenous zinc smelting slag, the EFs for As, Cd, Pb, Se and Zn are greater than 50 (representing extreme enrichment); the EFs for Hg and Cu, except for a few samples, range from 3 to 10 (moderate enrichment or moderate to severe enrichment); and the EFs for Cr, except for a few samples, range from 1 to 3 (slight enrichment). In the planting soil with slag, the EFs for As, Cd, Pb and Zn are all greater than 50 (extreme enrichment); the average EF for Se is 34.71 (severe enrichment); and the average EFs for Cr, Cu and Hg range from 1 to 3 (slight enrichment). In the planting soil without slag around the slag pile, the average EFs for Cr, Cu and Hg range from 1 to 3 (slight enrichment); the EFs for Cd, except for a few samples, range from 3 to 5 (moderate enrichment); the average EFs for Pb and Zn range from 3 to 5 (moderate enrichment); and the average EFs for As and Se are 7.43 (moderately severe enrichment) and 14.81 (severe enrichment), respectively. Therefore, the As, Cd, Pb, Se and Zn in the planting soil with and without slag are associated with different degrees of pollution, whereas most of Cr, Cu and Hg in the planting soil with or without slag are associated with slight pollution. Additionally, the As, Cd, Pb, Se and Zn in the slag are associated with extreme pollution, whereas the Cr, Cu and Hg in the slag are associated with different degrees of pollution.

### 3.5. Bioconcentration factors

The potatoes from the indigenous zinc smelting area are not enriched in the potentially toxic metal (loid)s. As indicated in Table 4, the average BCFs for As, Cd, Cr, Cu, Hg, Pb, Se and Zn in the potatoes are 0.0026 (ranging from 0.0001 to 0.0095), 0.0957 (0.0029–0.6170), 0.0008 (0.0002–0.0022), 0.0350 (0.0011–0.2232), 0.0095

(0.0009–0.0526), 0.0027 (0.0000–0.0439), 0.0352 (0.0035–0.1344) and 0.0317 (0.0007–0.1778), respectively, in the research area. The BCFs for the potentially toxic metal (loid)s in the potatoes are not higher than 1 in the research area. This result indicates that potatoes in the research area are not enriched in potentially toxic metal (loid)s and that the plants are able to avoid incorporating most of these elements to avoid potential harm. Moreover, in terms of the BCFs for As, Cd, Pb and Zn in the potatoes, the planting media are usually in the order of slag < planting soil with slag < planting soil without slag surrounding the slag pile, especially in terms of Cd, Pb and Zn.

### 3.6. Health risk index

As indicated in Table 5, the ADI values for As, Cd, Cr, Cu, Hg, Pb, Se and Zn in potatoes are less than 0.01 in the research area. Additionally, the HRI values are mostly lower than 0.1. However, the HRI values for As, Cd, Cu and Zn for men or women are close to or higher than 0.01, whereas the values for the remaining elements are less than 0.01 (Fig. 3). The HRI values for the potentially toxic metal (loid)s do not differ obviously among the potatoes grown in different planting media (the indigenous zinc smelting slag, planting soil with slag and planting soil without slag). Additionally, the HRI values for the potentially toxic metal (loid)s for men are usually lower than the corresponding HRI values for women.

### 3.7. Correlation coefficient

As shown in Table 6, positive significant correlations exist between the As, Cd, Cu, Pb and Se content in the planting media and the Se content in the potatoes in the indigenous zinc smelting area, and the correlation coefficients are 0.595, 0.579, 0.590, 0.624 and 0.628, respectively. A negative significant correlation exists between the Cr content in the planting media and the Se content in the potatoes (−0.609). The Cu content in the planting media shows positive significant correlations with the Cr (0.486) and Cu (0.488) contents in the potatoes. There is a positive significant correlation between the Hg content in the planting media and the Cr content in the potatoes (0.461). The pH of the planting media is positively and significantly correlated with the Pb content in the potatoes (0.464) and more positively significantly correlated with the Se content in the potatoes (0.730). There are no significant correlations between the other potentially toxic metal (loid) contents and the planting media pH or other

**Table 4**  
BCFs for potentially toxic metal (loid)s in potatoes in the indigenous zinc smelting area.

Planting media	Sample	As	Cd	Cr	Cu	Hg	Pb	Se	Zn
Indigenous zinc smelting slag	JMBTD	0.0001	0.0055	0.0015	0.0236	<b>0.0028</b>	0.0000	0.0574	0.0036
	CZPTD	0.0001	0.0040	0.0022	0.0109	0.0009	0.0001	0.0523	0.0016
	JZLMCTD	0.0004	0.0089	0.0010	0.0022	<b>0.0526</b>	0.0000	0.1344	0.0038
	CPTD	0.0008	0.0114	0.0006	0.0223	0.0067	0.0000	0.0138	0.0017
	YCLSJTD1	0.0002	0.0029	<b>0.0007</b>	0.0159	<b>0.0038</b>	0.0000	0.0035	0.0010
	CYTD2	0.0005	0.0069	<b>0.0004</b>	0.0218	<b>0.0054</b>	0.0000	0.0211	0.0015
	CYTD4	0.0005	0.0081	0.0008	0.0112	<b>0.0048</b>	0.0000	0.0581	0.0007
	FWJHTD	0.0001	0.0045	0.0007	0.0011	<b>0.0123</b>	0.0000	0.0228	0.0012
	XFTD1	0.0004	0.0073	0.0012	0.0156	0.0012	0.0000	<b>0.0059</b>	0.0012
	Average	0.0004	0.0066	0.0010	0.0138	0.0101	0.0000	0.0410	0.0018
	Planting soil with slag	LJPTD2	0.0004	0.0135	<b>0.0004</b>	0.0170	0.0059	0.0001	0.0154
CYTD1		0.0030	0.0654	<b>0.0002</b>	0.0149	<b>0.0076</b>	0.0001	<b>0.0125</b>	0.0095
YCLSJTD2		0.0022	0.0157	<b>0.0014</b>	0.2232	0.0063	0.0000	0.0400	0.0055
BJGTD		0.0015	0.0885	0.0006	0.0372	<b>0.0093</b>	0.0001	<b>0.0182</b>	0.0271
Average		0.0018	0.0458	0.0007	0.0731	0.0073	0.0001	0.0215	0.0112
Planting soil without slag	LJPTD1	0.0011	0.2836	0.0016	0.0250	<b>0.0053</b>	0.0018	<b>0.0273</b>	0.0655
	LSXZCTD	0.0095	0.6170	0.0004	0.0565	0.0088	0.0439	0.0400	0.1778
	HJZTD	0.0078	0.1250	<b>0.0003</b>	0.0380	<b>0.0119</b>	0.0003	<b>0.0222</b>	0.0404
	LSGTD	0.0078	0.2910	0.0005	0.0323	<b>0.0127</b>	0.0007	0.0800	0.1228
	YPZTD	0.0050	0.0655	<b>0.0006</b>	0.0534	<b>0.0077</b>	0.0003	0.0222	0.0773
	XFTD2	0.0074	0.1935	0.0002	0.0438	0.0146	0.0027	0.0222	0.0575
	Average	0.0064	0.2626	0.0006	0.0415	0.0102	0.0083	0.0357	0.0902
	Minimum	0.0001	0.0029	0.0002	0.0011	0.0009	0.0000	0.0035	0.0007
Maximum	0.0095	0.6170	0.0022	0.2232	0.0526	0.0439	0.1344	0.1778	
Average	0.0026	0.0957	0.0008	0.0350	0.0095	0.0027	0.0352	0.0317	

potentially toxic metal (loid) contents in the potatoes. These results show that 1) the Se content in the potatoes may be influenced by the As, Cd, Cr, Cu, Pb and Se contents in the planting media, 2) the Cr content in the potatoes may be affected by the Cu and Hg contents in the planting media, 3) the Cu content in the potatoes may be impacted by the Cu content in the planting media, and 4) the Pb and Se contents in the potatoes may be affected by the planting media pH.

**4. Discussion**

*4.1. Risk assessment of potentially toxic metal(loid)s in planting media*

As shown in Table 1, the As, Cd, Cu, Pb, Se and Zn contents of the planting soil without slag around the slag pile are all lower than those of the indigenous zinc smelting slag and the planting soil with slag, especially the Cd, Pb and Zn contents. In terms of the average contents of these elements, the planting media are usually in the order of slag > planting soil with slag > planting soil without slag around the slag pile. As described in Fig. 2, the PI values for As, Cd, Cu, Pb, and Zn in the indigenous zinc smelting slag and planting soil with slag are greater than 1, except for Cu and Pb in a few samples. The PI values for Cd, Cu and Zn in the planting soil without slag are greater than 1, except for Cu and Zn in a few samples. The PI values for the remaining elements are less than 1 in the indigenous zinc smelting area. Thus, in

terms of the PI values for As, Cd, Pb and Zn, the potato planting media are usually in the order of slag > planting soil with slag > planting soil without slag. Therefore, the As, Cd, Cu, Pb and Zn in the indigenous zinc smelting slag and planting soil with slag reach various levels of pollution. In particular, the concentrations of As, Cd, Pb and Zn in the slag and Cd and Zn in the planting soil with slag correspond to serious pollution. In the planting soil without slag, most of the Cd concentrations correspond to moderate pollution, while most of the Cu and Zn concentrations correspond to slight pollution. In terms of the pollution associated with As, Cd, Pb and Zn, the potato planting media are usually in the order of slag > planting soil with slag > planting soil without slag around the slag pile.

Additionally, the Cr, Cu and Hg in the planting soil with and without slag are mainly from naturally occurring sources, whereas the As, Cd, Pb, Se and Zn in the planting soil might be mainly from anthropogenic activities in the indigenous zinc smelting area. As shown in Table 3, in the indigenous zinc smelting slag, the EFs for As, Cd, Cu, Hg, Pb, Se and Zn are greater than 3, except for Cu in a few samples; and the EFs for Cr, except for a few samples, range from 1 to 3. In the planting soil with and without slag, the EFs for As, Cd, Pb, Se and Zn are greater than 3, except for Pb and Zn in a few samples; and the EFs for Cr, Cu and Hg range from 1 to 3, except for a few samples. The sources of potentially toxic metal (loid)s in topsoil can be determined through calculating the EFs of these elements (Hu et al., 2013; Peng et al.,

**Table 5**  
ADI and HRI values for the potentially toxic metal (loid)s in potatoes in the indigenous zinc smelting area.

	Planting media (Sample number)	As	Cd	Cr	Cu	Hg	Pb	Se	Zn
ADI for men (mg/kg/day)	Indigenous zinc smelting slag (n = 9)	1.33E-05	3.81E-05	1.38E-05	5.85E-04	1.57E-07	3.08E-05	2.50E-05	3.01E-03
	Planting soil with slag (n = 4)	1.13E-05	4.33E-05	6.42E-06	4.27E-04	1.28E-07	7.25E-06	3.21E-06	3.47E-03
	Planting soil without slag (n = 6)	1.14E-05	4.31E-05	1.07E-05	6.17E-04	1.50E-07	3.53E-05	3.21E-06	2.66E-03
ADI for women (mg/kg/day)	Indigenous zinc smelting slag (n = 9)	1.54E-05	4.41E-05	1.60E-05	6.75E-04	1.81E-07	3.56E-05	2.88E-05	3.48E-03
	Planting soil with slag (n = 4)	1.30E-05	5.01E-05	7.42E-06	4.93E-04	1.48E-07	8.38E-06	3.71E-06	4.01E-03
	Planting soil without slag (n = 6)	1.32E-05	4.98E-05	1.24E-05	7.13E-04	1.73E-07	4.08E-05	3.71E-06	3.07E-03
HRI for men	Indigenous zinc smelting slag (n = 9)	4.43E-02	3.81E-02	4.61E-03	1.46E-02	5.23E-04	8.81E-03	4.99E-03	1.00E-02
	Planting soil with slag (n = 4)	3.76E-02	4.33E-02	2.14E-03	1.07E-02	4.28E-04	2.07E-03	6.42E-04	1.16E-02
	Planting soil without slag (n = 6)	3.82E-02	4.31E-02	3.57E-03	1.54E-02	4.99E-04	1.01E-02	6.42E-04	8.86E-03
HRI for women	Indigenous zinc smelting slag (n = 9)	5.12E-02	4.41E-02	5.33E-03	1.69E-02	6.04E-04	1.02E-02	5.77E-03	1.16E-02
	Planting soil with slag (n = 4)	4.34E-02	5.01E-02	2.47E-03	1.23E-02	4.94E-04	2.39E-03	7.42E-04	1.34E-02
	Planting soil without slag (n = 6)	4.41E-02	4.98E-02	4.12E-03	1.78E-02	5.77E-04	1.17E-02	7.42E-04	1.02E-02



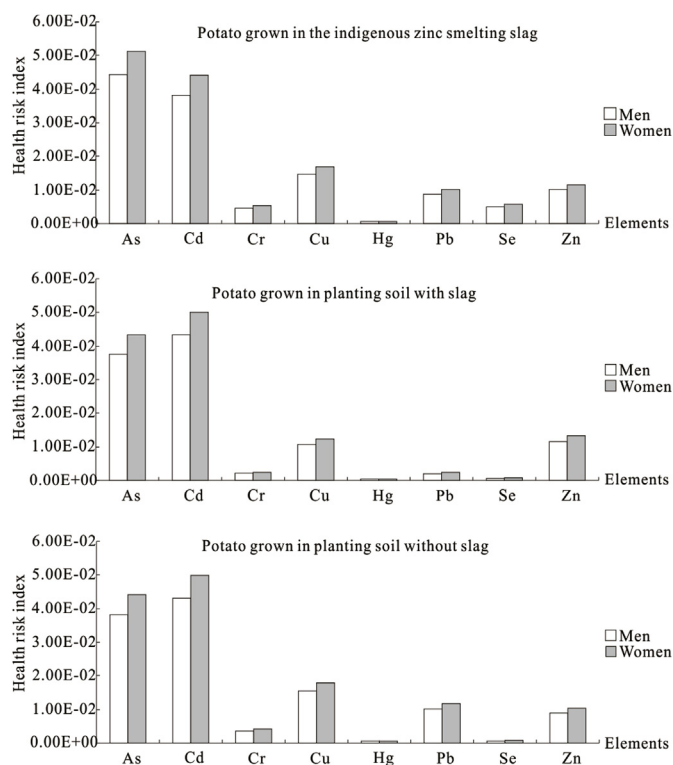


Fig. 3. HRI values for potentially toxic metal (loid)s in potatoes in the indigenous zinc smelting area.

2017). Although some elements in the soil originate mainly from the natural weathering of parent rocks (Peng et al., 2017; Yang et al., 2010, 2011a), anomalies are mainly affected by the specific natural geographical background (Yu et al., 2014) or by the effects of anthropogenic activities (Peng et al., 2017; Yu et al., 2014). The concentrations of potentially toxic metal (loid)s in the soil, especially in the topsoil, are easily affected by human activities (including the application of commercial fertilizers, sewage sludge and pesticides; mining activities; and production activities) (Peng et al., 2017). An *EF* that is less than or close to 1 indicates that the potentially toxic metal (loid) in the soil originates predominantly from natural sources (Hu et al., 2013). An *EF* greater than or close to 3 suggests that the soil has been polluted by human activities (Hu et al., 2013). Therefore, the planting soil with and without slag around the slag pile is slightly polluted with Cr, Cu and Hg, which are mainly controlled by natural sources and anthropogenic activities in the research area. As, Cd, Pb, Se and Zn have reached different degrees of contamination in the planting soil with and without slag and are mainly sourced from anthropogenic activities.

Therefore, attention should be paid to the monitoring and

Table 6

Spearman correlations of potentially toxic metal (loid)s in potatoes and their planting media in the indigenous zinc smelting area (n = 19).

	As P	Cd P	Cr P	Cu P	Hg P	Pb P	Se P	Zn P
As S	0.168	-0.287	0.284	0.074	0.105	0.384	0.595**	0.247
Cd S	0.151	-0.009	0.175	-0.067	-0.026	0.338	0.579**	0.044
Cr S	-0.068	0.242	0.144	0.097	0.079	0.020	-0.609**	0.027
Cu S	-0.199	-0.293	0.486*	0.488*	0.053	0.238	0.590**	0.118
Hg S	-0.042	-0.335	0.461*	-0.009	0.369	0.440	0.206	0.125
Pb S	0.153	-0.175	0.237	-0.053	0.132	0.464*	0.624**	0.081
Se S	0.026	-0.237	0.364	-0.040	0.106	0.469*	0.628**	0.076
Zn S	0.246	-0.372	0.183	-0.181	0.105	0.285	0.415	0.093
Al S	-0.191	-0.032	0.173	0.300	0.105	-0.136	-0.459*	0.177
pH	0.184	-0.326	0.380	0.101	0.066	0.464*	0.730**	-0.047

Note: \*\* Correlation is significant at the 0.01 level (2-tailed); \* Correlation is significant at the 0.05 level (2-tailed). A minus sign represents a negative correlation coefficient. An 'S' after the element indicates the element in the planting media, and a 'P' after the element indicates the element in the potatoes.

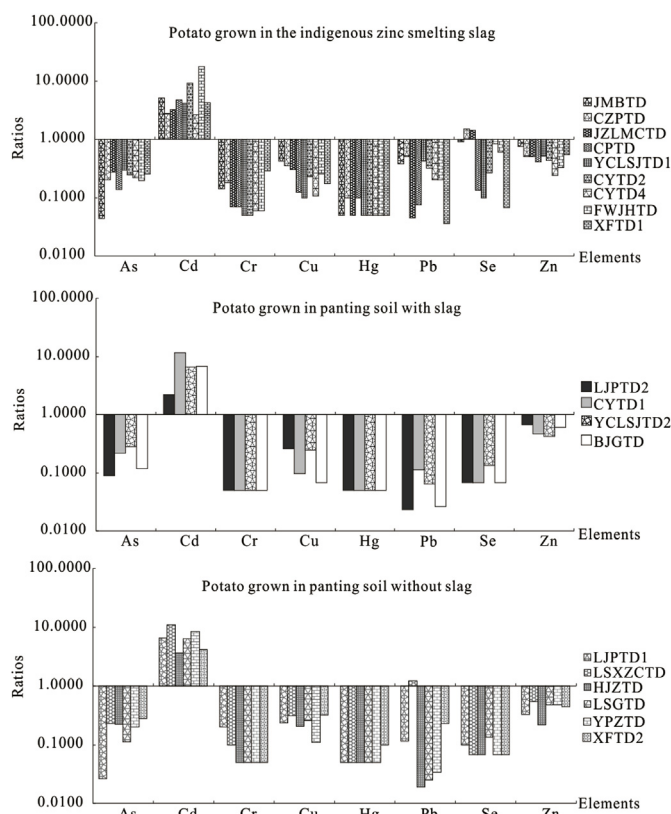


Fig. 4. Ratios between potentially toxic metal (loid)s concentrations in potatoes and their limit values in the indigenous zinc smelting area.

prevention of the potentially toxic metal (loid)s As, Cd, Pb, Se and Zn, especially in the slag and planting soil with slag in the indigenous zinc smelting area.

#### 4.2. Risk assessment of the potentially toxic metal(loid)s in potato

As illustrated in Fig. 4, compared with the limit values for potentially toxic metal (loid)s in food (MAPPC, 2005), only the Cd content in potatoes is higher than its limit value; the other elements, except for a few samples (Pb in sample LSXZCTD, Se in samples CZPTD and JZLMCTD), are all lower than their limit values in the indigenous zinc smelting slag. The Cd contents in potatoes in the research area range from 0.109 to 0.879 mg/kg, with an average value of 0.318 mg/kg (Table 2). These contents are similar to the Cd contents in potatoes in the Pb-Zn mining and smelting area of Huize County in Yunnan Province (Zou et al., 2014), Liupanshui City in Guizhou Province (Lang et al., 2013) and Weining County in Guizhou Province (Zhang et al.,

2017), which are all greater than the Cd limit value for potato. The range of Cd contents in potato in the Pb-Zn mining and smelting area of Huize County in Yunnan Province (Zou et al., 2014), Liupanshui City in Guizhou Province (Lang et al., 2013) and Weining County in Guizhou Province (Zhang et al., 2017) range respectively from 0.70 to 2.75 mg/kg, 0.07–1.01 mg/kg and 0.121–0.947 mg/kg (dry content, which was calculated on the basis of water rate and Cd content in fresh potato), with averages of 1.41 mg/kg, 0.33 mg/kg (the Cd contents in most potatoes are over the limit value) and 0.436 mg/kg, respectively. These results show that attention should be paid to the Cd contents in potatoes in areas with Pb-Zn mining, indigenous zinc smelting and high-Cd background values.

Moreover, the *ADI* and *HRI* values for potentially toxic metal (loid)s for both adult men and women are calculated to further evaluate the effects on residents' health in the research area due to the ingestion of potatoes. The *ADI* values for As, Cd, Cr, Cu, Hg, Pb, Se and Zn for both adult men and women are all below 0.01, and the *HRI* values are not higher than 0.1. The exposed population is considered to experience no significant risk when *HRI* < 1 (Cui et al., 2004; Khan et al., 2008; Rehman et al., 2017). Therefore, although the Cd content in the potatoes exceeds its limit value in the indigenous zinc smelting area and the planting media are seriously polluted with some potentially toxic metal (loid)s, the local residents have no health risks associated with eating potatoes.

#### 4.3. Cd absorption mechanism of potatoes

Although As, Cd, Pb, Se and Zn in the planting soil with and without slag around the slag pile have reached different degrees of contamination in the indigenous zinc smelting area, the potentially toxic metal (loid) contents in potatoes are not higher than the limit values, except for Cd (all samples) and Pb and Se (a few samples). Additionally, the Cd contents in planting media in the Pb-Zn mining and smelting area (Zou et al., 2014), Liupanshui City (Lang et al., 2013) and Weining County (Zhang et al., 2017), where the Cd contents in potatoes are similar to those from the research area, range from 4.68 to 46.88 mg/kg, 0.02–11.55 mg/kg and 0.41–10.0 mg/kg, with average values of 12.93 mg/kg, 1.17 mg/kg and 2.60 mg/kg, respectively. Moreover, the *BCFs* for the potentially toxic metal (loid)s are not higher than 0.5. This result indicates that the Cd content in the potatoes is not greatly affected by the Cd content in the planting media.

Additionally, in terms of the *BCFs* for As, Cd, Pb and Zn in the potatoes, the planting media are usually in the order of slag < planting soil with slag < planting soil without slag surrounding the slag pile. This order is especially obvious for Cd, Pb and Zn. The order in terms of *BCFs* for As, Cd, Pb and Zn in the potatoes is opposite that in terms of the *PI* values in the potato planting media. This might be caused by the special absorption and transfer mechanism of *Solanum tuberosum* L. Mclaughlin et al. concluded that the physiological processes of transport and distribution of Cd within *Solanum tuberosum* L. are the dominant factors (rather than uptake from the soil) in determining the content of Cd present in potatoes through a long-term growth experiment (Mclaughlin and Reid, 2004). Thus, the Cd content in a potato does not increase with increasing Cd content in the planting media, but the Cd content in the stem of *Solanum tuberosum* L. does increase significantly with increasing Cd content in the planting environment (Piotrowska and Kabata-Pendias, 1997). The Cd contents of *Solanum tuberosum* L. roots, stems and leaves are higher than those of the associated potatoes (Dunbar et al., 2003; Fu et al., 2014; Lin, 2017). In addition, the Cd content in potatoes is mainly sourced from the *Solanum tuberosum* L. roots rather than absorbed by the periderm of the potato (Reid et al., 2003). Dunbar et al. concluded that Cd movement into potatoes is from the soil to basal roots to shoots in the xylem and then back down to the tubers in the phloem (Dunbar et al., 2003). These studies indicate that *Solanum tuberosum* L. reduces the Cd content in the potatoes through increasing the Cd content in its roots, stems and

leaves. When the potato absorbs a certain extent of Cd, *Solanum tuberosum* L. does not transfer more Cd into the potato but keeps it in other parts (i.e., roots, stems and leaves) to avoid Cd damage to the potato. This process might be the main reason why there are similar Cd contents in potatoes that grown in planting media with a large range of Cd contents.

## 5. Conclusions

The order of the planting media in terms of the *PI* values for potentially toxic metal (loid)s As, Cd, Pb and Zn was generally as follows: indigenous zinc smelting slag > planting soil with slag > planting soil without slag surrounding the slag pile. Additionally, the Cr, Cu and Hg contents in the planting soil with and without slag surrounding the slag pile corresponded to slight pollution levels and were mainly derived from natural and anthropogenic sources. The As, Cd, Pb, Se and Zn contents in the planting soil with and without slag around the slag pile had different degrees of contamination and came mainly from anthropogenic sources. Therefore, attention should be paid to the monitoring and mitigation of these elements, especially in the slag and planting soil with slag in the indigenous zinc smelting area.

Considering the limit values for the eight elements in cereals, legumes, tubers and products (NY 861–2004), the Cd concentrations in the potato tubers exceeded the limit value throughout the entire study area, and the Pb and Se concentrations exceeded their limit values in most of the study area. Additionally, all the *BCFs* for the potatoes were below 0.5. This result showed that *Solanum tuberosum* L. is an excluder and is tolerant of the potentially toxic metal (loid)s As, Cd, Cr, Cu, Hg, Pb, Se and Zn because potato could isolate most potentially toxic metal (loid)s into other tissues to avoid harm from these elements. Moreover, the *HRI* values for the potentially toxic metal (loid)s through contaminated potato consumption were less than 0.1. Therefore, there is no significant health risk for either adult men or women in the indigenous zinc smelting area.

In summary, the crop concentrations of As, Cd, Pb, Se and Zn in the study area are of concern, and Cd in particular carries a higher risk and should be monitored. Thus, we suggest that potatoes can be planted in the study area but that the Cd content of the potatoes should be monitored. Additionally, although there is no significant health risk associated with the potentially toxic metal (loid)s As, Cd, Cr, Cu, Hg, Pb, Se and Zn, the contamination from other trace elements not investigated in the present study is still possible. Therefore, we suggest that other trace elements should be considered to ensure the safety of consuming crops grown in these polluted areas.

## Acknowledgements

This project was financially supported by the National Natural Science Foundation of China (Grant Nos. 41463009, 41563011, 41473027), the First Graduate Research Foundation of Guizhou Province (Contract No. QJYH-KYJJ-2016-05), the Public and Basic Geological Project of Guizhou Province (No. QGTZF-2015-34-4), the Foundation for Innovative Major Research Groups of the Education Bureau in Guizhou Province (QJH-KY-2016-024) and the Construction Project of the First-Class Subjects "Ecology" in Guizhou Province (GNYL [2017]007). We are very grateful to the anonymous reviewers for their helpful comments and constructive criticisms of both the English and the technical writing of this manuscript. We also thank American Journal Experts (AJE) for English language editing.

## Transparency document

Transparency document related to this article can be found online at <https://doi.org/10.1016/j.fct.2018.07.026>.

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