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## Accumulation Characteristics and Risk Assessment of Potentially Toxic Elements for Major Crops and Farmland Around A High-arsenic Coal Mine in Xingren, Guizhou, Southwest China

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### ABSTRACT

This study assessed the contamination by toxic elements (TEs), including lead (Pb), cadmium (Cd), chromium (Cr), zinc (Zn), copper (Cu) and arsenic (As), and their accumulation characteristics in soilcrop systems in Xingren, Guizhou, southwest China, by using the target hazard quotient (THQ) to evaluate the possible health risk in the target area. The mean value of the geo-accumulation index (Igen; 1.95, 1.89 and 1.96 for rice, maize and Coix lacryma-jobi L., respectively) shows As in partial contamination level. The potential ecological risk index (RI) values show that 90% of samples exceed in considerable ecology risk level (120 < RI 240). The concentration of investigated TEs (except Zn) in the edible part of the three crops tended to be lower than in other tissues: root > stalk > leaf > husk >edible part. Maize showed a major restriction in TE intake compared to rice and Coix lacryma-jobi L. The THQ of As was from 0 to 6.33 in all the plant samples, which indicates that the THQ exceeded the safe limit (THQ=1) in some samples. The total THQs (TTHQ) had a similar trend as RI, further indicating the potential health risk of the elements in combination. These data indicate that local people experience significant health risks if they ingest crops from the investigated area.

### INTRODUCTION

Toxic elements (TEs) are ubiquitously distributed in the pedosphere and the geosphere. Soil TE contamination is an environmental issue in China and worldwide (Sun et al. 2010) because of its adverse impacts, such as contamination of water and soil, phytotoxicity, biotoxicity, accumulative behaviour and potential human health risk (Yu et al. 2008). Eating plants from the contaminated area or inhalation of polluted particles are the principal factors contributing to TE exposure for the human population (Loutfy et al. 2006).

For instance, it has been recognised that the food chain can serve as an important pathway of TE exposure for humans and animals (Dudka & Miller 1999). TEs are likely to transfer and accumulate through the soil-crop system and thus may affect the quality of agricultural products and cause health risks to humans (Mico et al. 2006). Total TE content in soils is directly related to the background level, but anthropogenic activities seem to have the far-reaching impact (Singani & Ahmadi 2012). Anthropogenic activities, including mining, sewage irrigation and vehicular exhaust, are the major sources of TE pollution of farmland (Li et al.

2014). TE contamination in the vicinity of mining areas is mainly from smelting and refining, wastewater discharge and tailings disposal. Levels of TE pollution of air, water, sediments, soil and crops in the mine-affected areas are reported to be greatly higher than areas without mining activities (Balabanova et al. 2010, Razo et al. 2004, Liu et al. 2005, Liu et al. 2010, Bi et al. 2006).

Researchers worldwide have carried out studies of the distribution of TEs in different tissues of crops (Funtua et al. 2014, Hu et al. 2014, Rahman et al. 2014). TE accumulation in plants depends on plant species, plant tissues, TE species, the efficiency of different plants to take up metals and soil-to-plant bioaccumulation factors (Rattan et al. 2005, Liao et al. 2016). Wang et al. (2017) indicated that wheat was more likely to accumulate TEs than maize. Similarly, the TE contents in wheat and barley were higher than those in maize (Pruvot et al. 2006) and the mean value of TEs in rice was higher than maize in the edible part (Zarcinas et al. 2004). Chen et al. (2016) indicated that the transferability of Cu, Pb, Zn and Cd in a soil-rice system was stronger than those in soil-wheat and soil-canola systems. Cadmium had

a stronger transfer capacity from soil to crops and the root acted as a barrier for Pb uptake. The heavy metal uptake by plants shows the greatest accumulation of Cu, Cr and Pb in the roots, Cd in the leaves, and Zn in the seeds of rice (Fazeli et al. 1998). A large proportion of TEs easy accumulates in the metabolic organ, but a small amount accumulates in the vegetative organs. Nan et al. (2002) found that the order of translocation ratios of Cd and Zn in different tissues of maize and wheat were root > stem > grain. Therefore, the accumulative situation in crops was dissimilar among the investigated TEs.

A series of studies have been carried out in the Xingren coalmine area in southwest Guizhou province, China. Most studies have focused on the occurrence and enrichment of toxic elements in coals (Ding et al. 1999, Yang et al. 2006, Zhao et al. 1998, Yang et al. 2006), environmental geochemical characteristics (Yang & Liu, 1997, Qu et al. 2016), soil pollution and risk assessment in the vicinity of the mine (Qin et al. 2016) and water environment chemistry (Wu et al. 2009, Sun et al. 2013, Tang et al. 2009). Due to the exposure and accumulation of TEs, the health risk to local people is associated with crops grown in the polluted area. A study focused on the potential health risks of the TEs in soil and brown rice from Hunan province of China indicated that Cd had greater transferability from soil to the plant than other elements (Zeng et al. 2015). Meanwhile, the research shows that long-term exposure to TEs through brown rice consumption poses both potential non-carcinogenic and carcinogenic health risks to the local residents (Zeng et al. 2015). Nevertheless, due to the limited assessments of metal pollution and health risks in Xingren, research gaps remain between the TE levels and accumulation characteristics in soil-crop systems.

The objective of this study was to analyse the content of TEs in soil and crop tissues, to evaluate the soil toxic element pollution and to comprehensively understand the pollution of toxic elements in the study area. The representative farmland soil-crop (rice, maize and *Coix lacryma-jobi* L.) systems of Xingren were selected since they are the daily diet for the local people. The risk of crop intake was evaluated by the target risk coefficient, which provides a reference for the food safety of the residents in the mining area.

#### MATERIALS AND METHODS

#### Study Area

Xingren county (104°54′-105°34′E; 25°16′-25°48′N) is located in the southwest of Guizhou Province, China. This area has a subtropical humid climate with an annual average rainfall of 1300~1450 mm and monthly rainfall from May to October greater than 100 mm. The coal resource from the Xingren coalfield is plentiful and thus Xingren is listed as being one of 200 major coal-producing counties in China. The large numbers of high-coal mining operations caused environmental deterioration during the 1980s and 1990s. Although the mining activities in the high-arsenic coal area have been prohibited in 1994, there are still abandoned coalmines and coal gangue across the county. In particular, the acid wastewaters, which come into being through the migration of dust and rain leaching, are the main source of TE pollution for farmland. The major source of income for local residents is growing crops, which include rice, maize and *Coix lacryma-jobi* L., in the study area.

#### **Sampling and Preparation**

Sampling was carried out in October 2015. There were 67 sample sites and 8~10 soil and 3~5 plant samples were collected from each (Fig. 1). The soil was prepared by first randomly collected samples from a depth of 0-20 cm. All the samples were stored in clean polyethylene plastic bags to avoid further contamination and transported to the laboratory immediately. All soil samples were air-dried at room temperature (20-25°C). Stones, plant roots and other debris were removed and then the soil was sieved through a nylon sieve (pore size 2 mm). Crop samples were washed with purified deionised water (18.2 M $\Omega$ ·cm) and dried overnight at 105°C for 2 h, then at 75°C to a constant weight. After drying, the samples were crushed with a porcelain mortar and pestle and then sieved through a 2-mm nylon sieve. Portions of all samples were ground in an agate grinder and passed through a 0.149-mm sieve to further remove impurities. The prepared samples were stored in airtight Ziploc bags at 20°C for laboratory analysis.

#### Sample Testing and Quality Assurance

Soil samples (200 mg) were digested with 10 mL of concentrated  $HNO_3$ - $HClO_4$  in a 9:4 ratio at 160°C and then the levels of TEs (Pb, Cd, Cr, Zn and Cu) were determined. Additionally, As was extracted using 50 vol% aqua-regia [ $HNO_3$  (68 mass%): HCl (37 mass%) = 1:3]. Plant samples were put in an airtight polytetrafluoroethylene tube and acidic mixture ( $HNO_3$ - $H_2O_2$  in a 3:1 ratio) was added for digestion on a fully automatic digestion instrument (Mars 6, CEM, USA). The total TE (Pb, Cd, Cr, Zn, Cu and As) concentrations were determined by an atomic absorption spectrometer (ZEEnit700P®, Analytikjena, Germany). The instrumental parameters of the atomic absorption spectrometer for determination of Pb, Cd, Cr, Zn and Cu are given in Table 1 and the atomisation program is presented in Table 2.

Arsenic was analysed using an atomic fluorescence



Fig. 1: Sampling location and the study area site (I Soil/maize, II Soil/*Coix lacryma-jobi* L., III Soil/rice, IV Water, V Crops, VI Country, VII Tailings, VIII Road, IX coal mine).

spectrometer (AFS-933, Beijing Titan, China). The test conditions for As were: wavelength 197.3 nm; negative high voltage 270 V; total current 60 mA; complement cathodes 30 mA; atomiser height 8 mm. The digesting reagents were of analytical grade and purified deionised water (18.2 M $\Omega$ ·cm) was used for dilution.

The accuracy of the measurements was verified using the national standard reference materials from the National Research Centre (Beijing, China): GBW07405 and GBW07454 for soil samples; GBW07603 for plant samples. Addition one duplicate of five samples were used for quality control.

Blanks were used for background correction and control deviation of two blanks under 20%. The deviation of duplicate measurement results was within the tolerance range (<5%).

#### **Evaluation Methods**

**Geo-accumulation index:** The geo-accumulation index  $(I_{geo})$  was used to evaluate the degree of anthropogenic- or geogenic-induced accumulated pollution (Bhutiani et al. 2017). The index reflects the natural variation of the TE distribution and can estimate the impact of human activities on the environment.  $I_{geo}$  is widely used to investigate quantitative

Table 1: Instrumental parameters for atomic absorption spectrophotometry analysis for determination of TEs elements.

Demonstern	Element							
Parameter	Pb	Cd	Cr	Zn	Cu			
Wavelength (nm)	283.3	228.8	357.9	213.9	324.8			
Slit width (nm)	0.5	0.5	0.8	0.5	0.8			
Lamp type	HCl	HCl	HCl	HCl	HCl			
Lamp current (mA)	2	2	4	2	2			

Fable 2: Temperature programm	e for atomic absorpti	on spectrophotomet	ry for the detern	nination of TEs elements.
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		Pb			Cd			Cr			Zn			Cu	
Step	Temp °C	Ramp (S)	Hold (S)	Temp ℃	Ramp (S)	Hold (S)	Temp °C	Ramp (S)	Hold (S)	Temp ℃	Ramp (S)	Hold (S)	Temp °C	Ramp (S)	Hold (S)
Drying	110	5	10	110	6	20	110	5	10	110	5	10	110	5	10
Pyrolysis	800	300	10	500	300	10	1300	300	10	650	50	20	1100	300	10
Atomization	2000	1600	4	1500	1500	3	2300	1500	5	2150	1500	3	2100	1500	4
Clean-out	2450	500	4	2450	500	4	2450	500	4	2450	500	4	2450	500	4

indicators of TEs pollution in sediments and soil (Förstner et al. 1993). The formula is:

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

Where,  $I_{geo}$  is the index of geo-accumulation for an element in soil samples; and are the determined concentration of the metals in the target and reference areas, respectively. The values used were the average background values of TEs in Guizhou soil: As = 20.00 mg/kg, Cr = 95.90 mg/kg, Pb = 35.20 mg/kg, Zn = 99.50 mg/kg, Cd = 0.66 mg/kg and Cu = 32.00 mg/kg (MEPPRC 1990). I<sub>geo</sub> and the classification of pollution level (Müller 1969) are given in Table 3.

**Potential Ecological Risk:** The Potential Ecological Risk Index (RI) evaluates the ecological degree for toxins and toxic elements in soils (Häkanson 1980) that could be toxic for biological species (Yisa et al. 2012). As one of the most common risk assessment methods of toxic element pollution for soil, it not only reflects the impact of a single pollutant in a particular environment but also reflects the comprehensive impact of a variety of pollutants. The formulas are shown as follows:

$$E_r^i = T_r^i \cdot \frac{C_i}{C_n^i} \qquad \dots (2)$$

$$RI = \sum E_r^i = \sum T_r^i \cdot C_f^i \qquad \dots (3)$$

Where, is the pollution coefficient for a certain element, which reflects the pollution level of a single TE (Zhuang & Gao 2014). is the concentration of the *i*th toxic metal in soil, and indicates the reference background concentration of toxic elements in the soils of Guizhou Province (MEP-PRC 1990). is the potential ecological risk coefficient of the particular TE. is the toxic-response factor for element *i*. According to Häkanson (1980), is set as follows: Pb = 5, Cd = 30, Cr = 2, Zn = 1, Cu = 5 and As = 10. The potential ecological risk index was classified into five categories (Table 4) (Häkanson 1980, Zhuang & Gao 2014).

There were some differences with the classical Häkanson potential ecological hazard index method (Häkanson 1980). In the studies of Häkanson (1980) and Zhuang & Gao (2014), the first-stage upper limit of the is obtained by the non-polluted pollution coefficient (= 1) multiplied by the maximum toxicity coefficient in the reference pollutant. In this paper, the value of Cd is the largest one among the six of TEs, as = 30. From this, the first grading criterion of is 30, and the other criterion is multiplied by 2 on the previous stage (Li et al. 2015).

From Formula (3), RI is related to the type and quantity of pollutants. Specifically, the pollutants constituted more complex have stronger toxicity (the larger ), the greater the RI value. Thus, it must be considered that appropriate adjustment the type and quantity of pollutants when using the RI ecological risk assessment.

Using Häkanson's first-level classification limit (150) and the total toxicity factor of eight pollutants (133) to get the unit toxicity coefficient (1.13). Taken unit toxicity coefficient (1.13) to multiply total toxicity coefficient (53) of six TE, and round the decimal to get the first limit of RI (about 60), the other criterion was multiplied by 2 on the previous stage. The classification criteria for the assessment of the potential ecological risk of TEs in soils are given in Table 4. It is different from the Häkanson's classification.

Plant enrichment is closely related to plant species, soil substrate, and TEs' categories. The bioaccumulation factor or transfer factor (BAF/TF) is usually used to characterise plant TE accumulation (Khan et al. 2010), which reflects the plant ability for metal storage in roots and/or translocation to aerial organs. The BAF was calculated as follows:

$$BAF = \frac{C_r}{C_s} \qquad \dots (4)$$

Table 3: Index of Geo-accumulation  $(I_{geo})$  and classification of pollution level (Müller 1969).

Degree of pollution	Clean	Light Pollution	Partial contamination	Contamination	Emphasis on pollution	Heavy pollution	Serious pollution
Igeo	$I_{geo} \le 0$	$0 < I_{geo} \le 1$	$1 < I_{geo} \le 2$	$2 < I_{geo} \leq 3$	3< <i>I<sub>geo</sub></i> ≤4	$4 < I_{geo} \le 5$	I <sub>geo</sub> >5
Grade	0	1	2	3	4	5	6

Table 4: Grading standards of potential ecological risk of TEs in soils.

Degree	Low	Moderate	Considerable	High	Very hight
Ei r	≤30	30~60	60~120	120~240	≥240
RI	60	60~120	120~240	≥240	

$$TF = \frac{C_{t}}{C_{r}} \qquad \dots (5)$$

Where,  $C_t$  represents the TE concentration in tissues (stalk, leaf, husk or edible parts) of crops;  $C_r$  represents the concentration in the root;  $C_s$  represent concentration in soils on a dry-weight basis.

The target hazard quotient (THQ) is a health risk assessment model recommended by the US Environmental Protection Agency (US EPA 1997). The health risks from consumption of crops depend on the level of exposure and the amount of absorption by local inhabitants. The estimated risk using the THQ is based on the equation below (US EPA 1997, Bhatti et al. 2017).

Where,  $C_C$  is the metal concentration in crops (mg/kg);  $D_F$  is food ingestion (g/person/d);  $B_W$  is the average adult body weight (60 kg); RfD is the oral reference dose (mg/kg/d).

$$THQ = \frac{C_{crop} \times D_{foodintake} \times EF \times ED}{B_{W} \times AT \times RfD} \qquad \dots (6)$$

Where,  $C_{crop}$  is the metal concentration in food (mg/kg);  $D_{food intake}$  is food ingestion (g/person/d); BW is the average body weight, adult (60 kg); EF is exposure frequency (365 days/year); ED is exposure duration (70 years); AT is averaging time for noncarcinogens (365 days/year × number of exposure years, assuming 70 years in this study); RfD is the oral reference dose (mg/kg/d). Oral reference doses were  $3.5 \times 10^{-3}$ ,  $1.0 \times 10^{-2}$ , 1.5, 0.3,  $4.0 \times 10^{-2}$  and  $3.0 \times 10^{-4}$  mg/kg/d for Pb, Cd, Cr, Zn, Cu and As respectively (US EPA 1997).

Considering the literature (US EPA 1997, Bhatti et al. 2017, Fang et al. 2015, Du et al. 2013, Zeng et al. 2015, Wang et al. 2016) and the US EPA exposure factors handbook, it was determined that the adult intake in this area was 0.25, 0.15 and 0.20 kg/person/d for rice, maize and *Coix lacryma-jobi* L., respectively. If the THQ is  $\geq$  1, the exposed population is likely to experience serious health risks and if the level of the THQ is < 1, the risk associated with exposure to the metal is negligible.

The potential impact of TEs on human health is generally a combined effect of a variety of elements (Bhatti et al. 2017).

Table 5: pH and variation coefficient (VC) of TEs in soil samples.

To assess the combined effect of more than one element, Total THQ (TTHQ) is calculated by the following modified equation (US EPA 1997):

 $TTHQ(crop) = \sum THQ_{M} = THQ_{M1} + THQ_{M2} + \dots + THQ_{Mn} \dots (7)$ 

When TTHQ  $\leq 1$ , it means there is no significant negative impact; when  $1 \leq \text{TTHQ} < 10$ , the TEs may be potential non-carcinogenic health risks, and when TTHQ > 10, the presence of TEs will cause chronic toxic effects.

The data were processed in Excel 2007 for preliminary data processing. Statistical analyses were performed with the Statistical Package for the Social Sciences (SPSS 18.0). Charts and graphs were created using Origin (Origin 8.5, OriginLab) and The R Programming Language (R i386 3.4.1).

#### **RESULT AND DISCUSSION**

#### **Concentration of TEs in Crop Soils**

The soil pH varied between 3.95 and 6.37. The rice soil had lower pH compared to the two other crops. Table 5 summarises the pH and variation coefficient (VC, SD/mean) of Pb, Cd, Cr, Zn, Cu and As in soils from the target area. According to the soil background value of Guizhou (MEPPRC 1990), all elements in the soil were higher than the background value, especially Pb and As. The mean concentrations of Pb (183.11 mg/kg) and As (119.03 mg/kg) in rice soil were 5.2 and 5.95 times higher than the background value (Pb = 35.20) mg/kg, As = 20.00 mg/kg), respectively. Similar results were found for maize and Coix lacryma-jobi L. The Cd and As minimum concentrations in soils exceeded the grade II of environmental quality standard values (Cd = 0.30 mg/kg, As =30 mg/kg in paddy field or 40 mg/kg in dry land) for soils of China (MEPPRC 1990); in particular, the As in paddy soil was 2.45 times above the standard value.

The mean value of Pb, Cd, Cr, Zn, Cu and As in soil exceeded the maximum permitted levels (Fig. 2). The concentrations of Pb, Cd and As were found to be far more than the reported levels (Shen et al. 2011) in the target area, while Zn and Cu showed less difference. One reason is that the investigated area suffered sewage irrigation, as well as spraying of pesticides, manure and fertiliser, which possibly increase

Soil usage type	pH	Statistics	Pb	Cd	Cr	Zn	Cu	As
Rice soil (n=22)	3.95~6.19	VC/%	29.74	20.95	16.41	9.63	30.72	23.13
Maize soil (n=22)	4.28~6.22	VC/%	22.37	22.82	17.28	11.77	38.90	22.20
Coix lacryma-jobi L. soil (n=24)	4.35~6.37	VC/%	18.80	21.34	17.39	13.48	42.89	25.80

the TE contamination compared to that of abandoned agricultural land. Another possible reason is the mining activities and factories around the study area (Li et al. 2014), which may also contribute to the TE exposure. The mean levels of Pb, Cd, Cr, Zn and Cu in the three crops were in this order: upland (207.89, 0.89, 194.00, 102.52 and 131.43 mg/kg for maize; 212.18, 0.88, 197.31, 106.40 and 128.01 mg/kg for *Coix lacryma-jobi* L.) > paddy soil (183.11, 0.78, 188.73, 97.22 and 147.10 mg/kg). These five elements had similar trends in the maize soil and the *Coix lacryma-jobi* L. soil.

#### Assessment of TE Pollution by the Index of Geoaccumulation:

The geo-accumulation indexes calculated for the soil of the target areas are shown in Fig. 3. The mean  $I_{geo}$  for toxic elements had a trend of As and Pb > Cu > Cr > Cd > Zn. A similar study by Qin et al. (2016) indicated that As and Pb had relatively higher contamination levels ( $I_{geo} \ge 3$ ). The result from Fig. 3. showed that Zn from all the soil samples was similar to the unpolluted level, Cd (86.36% soil samples for

rice, 76.19% soil samples for maize, 79.17% soil samples for *Coix lacryma-jobi* L.) was at the clean level and Cr (90.91%, 90.48% and 95.83% for rice, maize and *Coix lacryma-jobi* L.) indicated light pollution, while Pb, Cu and As indicated moderate contamination. According to the mean  $I_{geo}$ , the elemental concentration in the studied soil samples could be categorised as: (1) As, Pb and Cu in the moderately polluted category; the source could be coal gangue, which contains Cu and Pb, and uncontrolled discarded wastewater (Qishlaqi et al. 2008); (2) Cr was in the lightly polluted category and might be mainly related to atmospheric deposition (Shi et al. 2014, Zeng & Wu 2013); and (3) Cd and Zn were in the unpolluted category. The results are similar to those reported by Qin et al (2016) in which the contamination levels were in the order: As, Pb and Cu > Cr > Cd.

# Assessment of TE Pollution by Potential Ecological Risk

According to the formulas (2-3), the ecological risk (ER) value and potential ecological risk values (RI) for each of



Fig. 2: Box plots for content of TEs in different type soils. (n=67) Guizhou soil background: As=20.00mg/kg, Cr=95.90mg/kg, Pb=35.20mg/kg, Zn=99.50mg/kg, Cd=0.66mg/kg, Cu=32.00mg/kg. Standards values (pH <6.5) were 250, 0.30, 200, 50 mg/kg for Pb, Cd, Zn and Cu; 250, 30 mg/kg for Cr and As in paddy field, 130, 40 mg/kg for Cr and As in dry land. (Grade II of environmental quality standards values for soils of China, GB 15618-1995).



Fig. 3: Box plots for  $I_{geo}$  of TEs in different type soils, the horizontal lines represent  $I_{geo}$  values of -1, 0, 1, 2 and 3. (n=67).

the studied metals are shown (individually and in total) in Fig. 4 and 5. The risk indices of the metals are in the order: As > Cd > Pb > Cu > Cr > Zn.

The ER values for Cr and Zn were mostly at low levels, while these values were high for the other examined elements. The results indicate that the contribution of Cr and Zn to the potential ecological risk is relatively low. The sample of ER<sub>Pb</sub> in low ecological risk level (50% of samples) and moderate ecological risk level (50% of samples) is in equal possibility. Almost every sample of ER<sub>Cu</sub> was of low potential ecological risk. From Fig. 3, almost all the ER<sub>As</sub> and ER<sub>Cd</sub> values from the study area reached the level of moderate potential ecological risk (30 < ER < 60).

The  $I_{geo}$  result indicates that Pb and As are in a similar pollution situation. The reason why  $\text{ER}_{As} > \text{ER}_{Pb}$  is that the toxic-response factor of As is double that of Pb. Cadmium posed a moderate potential ecological risk, which differs from the  $I_{geo}$  level because the toxic-response coefficient is

relatively high (= 30). The rank of the ER average of each element in the three types of land-use was similar to the results of  $I_{eeo}$ , indicating that the soil pollution impacts its ER.

Fig. 5 shows that nearly 94% of the study area reached the level of considerable potential ecological risk (120 < RI < 240). The variation decreased in the order: maize (100-205) > rice (97-196) > *Coix lacryma-jobi* L. (117-195). Average RI was highest in *Coix lacryma-jobi* L. followed by maize and rice. The mean and individual values showed considerable potential ecological risk due to a high level of TEs in the study area. The interaction of the six elements increases the risk of the study area and the high degree of potential ecological risk may lead to crop contamination.

It is crucial to integrate these methods to obtain more knowledge of the TEs risk in the target area due to the limitation of the current models (Zhang et al. 2012). Long-term mining activities (> 10 years) resulted in high arsenic levels in coalmining areas (Chen et al. 2002), which polluted the



Fig. 4: The ecological risk (ER) of HMs in soil samples, the horizontal lines represent ER values of 30, 60 and 90. (n=67 soil, rice is range 1 to 22, maize is 23 to 43, *Coix lacryma-jobi* L. is 44 to 67).

nearby water and affected ecological functions. There was moderate contamination by As and the considerable potential ecological risk is shown by merging the results of  $I_{geo}$  and the potential ecological risk.

#### Assessment of TE Concentration in Crops

The concentration of TEs in each plant portion is presented in Fig. 6. TEs were widely distributed in different parts of the plant and the TEs in root were significantly higher than in other parts (Bose & Bhattacharyya 2008). It is important to focus on the TE content of the edible part because it is the main source of dietary exposure (Khan et al. 2015). The mean concentration of Pb (0.12 mg/kg), Cd (0.07 mg/kg), Cr (0.64 mg/kg), Cu (1.58 mg/kg) and As (0.17 mg/kg) in the edible part of rice were less than other organisation (the minimum of other organisation: 0.75, 0.08, 1.44, 1.80, 0.65 mg/kg). Similar results were found in maize and *Coix lacryma-jobi* L.

Analysis of the levels of the elements in three crops (rice, maize and Coix lacryma-jobi L.) showed that TEs (except Zn) were highest in the root and lowest in the edible part. However, Zn showed a different trend. Zn was higher in the stalk and leaf for rice, in the leaf and husk for maize, and the leaf and edible parts for Coix lacryma-jobi L. Compared with rice and maize, the edible part of Coix lacryma-jobi L. has a relatively strong capacity for Zn storage. According to the maximum permitted level of contaminants in food set by the Ministry of Heath of the People's Republic of China (MHPRC 2012), the mean value of the edible portions of the three crops was below the threshold of safety value for Pb, Cd, Cr, Zn, Cu and As (0.20, 0.10, 1.00, 50.00, 10.00 and 0.20 mg/kg). The concentrations of Pb in the edible part were highest in Coix lacryma-jobi L. (0.14 mg/kg) and lowest in maize (0.10 mg/kg), which was similar to

Cr and As. Zinc was highest in *Coix lacryma-jobi* L. (10.91 mg/kg) and lowest in rice (6.24 mg/kg), which was the same as Cd and Cu.

Compared TEs content of three crops show that As and Cd were highest (lowest) in rice (maize) and maize (rice), respectively; Cu was higher in *Coix lacryma-jobi* L. There was an interspecific difference among crops. As and Pb content was high and matched the geo-accumulation index evaluation result. Compared to the concentration of Cd in soil, the concentration in crops was at a higher level.

#### The TF and BAF of the Crops

To assess the transfer of TEs from soil to crops, the transfer factor (TF) and bioaccumulation factor (BAF) were calculated (Fig. 7). The BAF and TF of different TEs in crops were dissimilar. The capacity of plants to uptake toxic elements is different and the same toxic element can be accumulated in different ratios in various plant species (Singh et al. 2010). The transport and enrichment ability of TEs was higher in the aerial parts than the underground parts of the crops. The reason is that aerial parts of plants mainly consist of metabolic organs and biomass is higher than underground.

Transfer factors of the edible parts (leaf, stalk and husk) for TEs decreased in the order Cd > Zn > Cu > Cr > As > Pb. The TF<sub>Pb</sub> values (except above total) was lower than 0.01 for the three cultivation systems. The possible reason was that the root hinders uptake of Pb (Cui et al. 2014). The BAF<sub>root</sub> (except As of maize and Pd of *Coix lacryma-jobi* L) decreased in the order Cd > Cu > Zn > As > Cr > Pb, which is similar to the study by Chen et al. (2016) in rice of the Yangtze River Delta region. The TF<sub>Zn</sub> and TF<sub>As</sub> of the aerial part (except As of rice) were in contrast to those of the root (Zn > Cu and Cr > As). This result shows that the aerial parts



Fig. 5: The potential ecological risk index (RI) of TEs in soil samples, the horizontal lines represent RI values of 60, 120 and 180. (n=67 soil, rice is range 1 to 22, maize is 23 to 43, *Coix lacryma-jobi* L. is 44 to 67.)

could absorb the Zn by the root and hinder the migration of As. BAF (TF) of Cd was significantly higher than other elements. Cd performed a higher capacity of transportation inside the plant and the soil-crop system, which may explain that why soil evaluated in clean level has a potential risk. These results indicate that despite Cd in soil was not polluted  $(I_{peo} < 0)$ , but the ability of three crops for the absorption of Cd was relatively strong. BAFs of Zn were slightly lower than those of Cd. The synergism between Cd and Zn enhances the efficiency of each other's transfer (Nan et al. 2002). In the rice-soil system,  $\mathrm{BAF}_{\mathrm{Zn}}$  and  $\mathrm{BAF}_{\mathrm{As}}$  showed the highest values, which were different depending on the soil type (dry land > paddy field). These data indicate that the accumulation of TEs in crops is not only influenced by soil concentration, but also by physical and chemical properties of the soil or other factors. For instance, the equilibrium pH value (<4) could affect toxic elements sorption and desorption on soil components thus affecting the migration of metals (Najafi & Jalali 2015). Most soils of the target area are acidic, which may promote the migration of toxic elements from soil to crop (Chen et al. 2016). Possible reasons include (1) rice having a strong transferability for Zn and As; (2) water evaporates out cause the pH to decrease during the maturation period (Shamshuddin et al. 2014), which may lead to metal desorption and metal ions being released into the soil solution (Chen et al. 2016).

The BAF and TF of each metal were dependent on the crop type and species. The bioaccumulation of toxic elements is different for different plant species, which is reflected by differences in their growth, reproduction, occurrence and survival in the metal-contaminated soil (Khan et al. 2015). Notably, different plant species possess different tolerance to the same pollutant under the same conditions. This difference may be explained by the different mechanisms and efficiency in the elemental uptake of plant species (Garty 2001). The BAF (TF) of TEs (except for Zn) in the three crops can be divided into three levels: root > stalk and leaf > husk and edible parts, while the Zn is disordered. Fig. 6 shows that the accumulation ability of edible part is highest in Coix lacryma-jobi L (except Cr) compared to other crops. The TF of As in each part of rice is higher than other crops in this study, which represent that As was easily absorbed by



Fig. 6: The concentrations of TEs in each part of crop samples (mg/kg).

the rice. Maize had relatively lower enrichment and transport capacity compared to rice and *Coix lacryma-jobi* L, except for Cd. Combining the BAF and  $TF_{above total}$  it was found that the absorption of Cu (Zn) of *Coix lacryma-jobi* L. (rice) was higher than other plants.

# Correlation Coefficient Between TEs in Soil and Crop Tissue

As shown in Fig. 8, the r-values were found to be significant

(p<0.05). Thus, all the observed correlations were not high. The *r*-value depicted the strongest positive correlation as being between root and soil. The most significant positive correlation was observed for As of rice, Cu of maize and Zn of *Coix lacryma-jobi* L. (*r*-values of 0.415, 0.437 and 0.413, respectively). TEs in root were positively correlated with soils, showing an increase in the concentration of one metal with a decrease in the concentration of other metals. No significant positive or negative correlation was observed



Fig. 7: Transfer factor and bioaccumulation factor of TEs in the three soil-crop systems.



Fig. 8: r-values distribution between TEs contents in soil and different tissues of plants.

in other parts of the plants, which indicates that the sources of the elements in the soil were not the same.

#### Health Risk Assessment of TEs through the Food Chain

Target hazard quotient through the food chain quantification health risk, and the assessment process main determined by exposure to various virulence factor (Bhatti et al. 2017). The THQ is a tool to assess the level of risk associated with a particular pollutant. The estimation of the hazard quotient of metals in different crops from various sites is given in Table 6.

In the entire study area, the THQs for TEs through food (crops) consumption were found to be in the order: As > Cd > Cu > Pb > Zn > Cr (except *Coix lacryma-jobi* L.). The THQ values in this study were <1 for all TEs expect As. The THQ<sub>As</sub> in rice, maize and *Coix lacryma-jobi* L. was  $0 \sim 6.33$ ,  $0 \sim 1.22$  and  $0.56 \sim 3.03$ , respectively, which indicates that some samples' THQ was >1 and above the safe limits. The mean value of THQ<sub>As</sub> for maize was <1 (Table 6), while those of rice and *Coix lacryma-jobi* L. were >1. The results display similar trends with the BAF and TF (rice > *Coix lacryma-jobi* L. > maize). It is critical to reduce BAF and TF to ensure food safety.

The ranking orders of TTHQ for each plant were rice > *Coix lacryma-jobi* L. > maize. The potential risk of consumption of rice in the target area is higher than the others. The TTHQ of crop species was  $\geq$  1, indicating potential non-carcinogenic risks from ingestion of local crops (rice, maize and *Coix lacryma-jobi* L.). Since the THQ was <1 for TEs in maize, the health risk could be negligible to the inhabitants of the studied area by individual TE, but the combined effect of the metals may pose a health risk. The estimated TTHQ was mainly due to As. The THQ accounted for 76.77% (rice), 62.86% (maize) and 66.14% (*Coix lacryma-jobi* L.) of the TTHQ.

#### CONCLUSIONS

TE content in the investigated agricultural soils were in the order As > Pb > Cu > Cr > Cd > Zn. The average TE values were greater than the respective background values of the local area, while the soil contamination content exceeded the national standard.

The results of  $I_{geo}$  signify that As was at the highest contamination level compared to other TEs, while Pb and Cu were at the moderately polluted level, Cr was in the lightly polluted level, and Cd and Zn were not pollutants. The results of RI showed that exceeding 90% soil sample point is in the considerable potential ecological risk level, especially soil growing *Coix lacryma-jobi* L., and the highest contributing element was As. Therefore, urgent measures must be taken to control contamination with As in this area.

The  $\text{TF}_{Cd}$  value was significantly higher than other elements, while Pb was second highest. There was competition in transport and absorption between Pb and Cd. Comparing the three plants, As was easily absorbed by the rice, while Cd was easily absorbed by maize and Cu was easily absorbed by *Coix lacryma-jobi* L. Pb, Cd, Cr and As are accumulated in rice, indicating that rice (compared maize and *Coix lacryma-jobi* L.) has a strong capability to transfer these metals from root to grain. Maize shows lower intake of TEs compared to rice and *Coix lacryma-jobi* L., while rice enriched the toxic elements.

The TTHQs values for the target area were  $\geq 1$ , which indicates potential health risks. Therefore, measures must be taken to cut down the contents of TEs in the grain and soil and to use new technology to remove or reduce pollution due to anthropogenic activities.

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Storm	Statistics		TTUO					
Stem	Statistics	Pb	Cd	Cr	Zn	Cu	As	TIHQ
	Minimum	0.03	0.02	1.03×10 <sup>-3</sup>	0.07	0.11	0.00	0.23
Rice	Maximum	0.27	0.92	3.39×10 <sup>-3</sup>	0.15	0.20	6.33	7.88
	Mean	0.15	0.30	1.78×10 <sup>-3</sup>	0.09	0.16	2.30	3.00
	Minimum	0.03	0.00	4.10×10 <sup>-4</sup>	0.04	0.08	0.00	0.14
Maize	Maximum	0.16	0.33	5.33×10 <sup>-4</sup>	0.07	0.25	1.22	2.02
	Mean	0.07	0.21	4.69×10 <sup>-4</sup>	0.06	0.16	0.84	1.33
	Minimum	0.06	0.02	$1.04 \times 10^{-3}$	0.09	0.24	0.56	0.97
Coix lacryma-jobi L.	Maximum	0.32	0.45	1.39×10 <sup>-3</sup>	0.17	0.50	3.03	4.47
	Mean	0.13	0.28	1.11×10 <sup>-3</sup>	0.12	0.38	1.79	2.70

Table 6: THQ and TTHQ values for TEs caused by the consumption of crops.

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