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Evaluating Health Risk Indicators for PTE Exposure in the Food Chain: evidence from a Thallium Mine Area

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Abstract: Thallium (Tl) has a high relative toxicity and is easily taken up by plants but little is known about wider relationship with co-contaminants and in typical domestic food crops. We evaluated the extent of contamination, evidence for bioaccumulation in typical food crops (Chinese cabbage, green cabbage, chili, carrot, corn and rice) and subsequent contribution to health risks for 7 elements (Tl, As, Cd, Pb, Ni, Cu, Zn) associated with soil contamination in the local soils of a major Tl mine in Guizhou, southwest China. Derivation of relevant risk indicators from the bioconcentration factor (BCF), comprehensive crop pollution index (P), the target hazard quotient (THQ) (element) and the hazard index (HI) (all elements) were assessed as tools to support the evaluation. Our results showed that the degree of contamination and uptake by crops in the study area were: root vegetables > leaf vegetables > fruit vegetables > cereals. With the exception of corn, other crops pose a significant risk to human health which is dominated by the Tl content. In addition the Cu in carrot samples suggests hyper accumulation at the site and poses a high risk to human health. The results provide direct evidence of significant food chain exposure and identifies the need for Tl-focused management of soil/plant interaction and that strategy needs to also understand the implications for behavior of co-contaminants in the area.

Keywords: Potentially Toxic Elements (PTEs); thallium mine area; crop; bioconcentration factor; health risk assessment

1. Introduction

The effect of long-term mining frequently leads to the extensive localized pollution of soil systems by a specific range of potentially toxic elements (PTEs) associated with the particular ore deposit (Chen et al. 2015). The PTEs entering the soil are not biodegraded and persist and accumulate in the soil system and are potentially transferred into the crops over many seasonal cycles (Adama et al. 2014). This provides a potential pathway directly to the human body through the food chain (Amin et al. 2013). Excessive intake of trace elements, such as copper (Cu), zinc (Zn) and nickel (Ni), which are essential for human metabolism, will cause toxic effects and for non-essential elements such as cadmium (Cd), chromium (Cr) and lead (Pb), small additional intake can be harmful to human health (Bermudez et al. 2011; Gall et al. 2015; Zheng et al. 2015). The impact of increased exposure and ingestion has been identified to cause a variety of health problems. In our case the elements thallium, arsenic, cadmium, lead, nickel, copper and zinc are of local concern, associated with specifc mineralization and commercially viable ore exploitation. Thallium (Tl) can cause cardiovascular disease, blindness and hair loss (Wappelhorst et al. 2000; Peter et al. 2005); Arsenic (As) can cause vascular diseases, neurological disorders, dermal lesions and skin cancer (Patlolla et al. 2012; Tan et al. 2016); Cd can lead to lung cancer, prostatic hyperplasia, renal dysfunction and fractures (Wu et al. 2018); Pb can cause damage to neuroskeletal endocrine and immune systems (Pareja-Carrera et al. 2014; Grégoire et al. 2013); Excessive intake of Cu can affect liver and kidney function, the central nervous system, cause depression and even lung cancer (Chen et al. 2018; Ji et al. 2013). So the question arises—at what point does 'hazard become a significant risk? Consequently an effective approach to health risk assessment in mining disrupted soil environments is of real practical significance, particularly for communities utilizing land for domestic crop production.

Soil exposure (ingestion, dermal contact and inhalation of PTEs in soil), contamination of drinking water and food crops are major pathways for human exposure to PTEs (Chen et al. 2018). A number of studies have identified that consumption of food crops contaminated with PTEs has been demonstrated to be the major route for human exposure (Bermudez et al. 2011; Ji et al. 2013; Khan et al. 2008). In addition, many health risk assessment studies have focused on a single category of food which underestimates risk from the total "food basket" for residents contaminated environments. For instance, Li et al. (2018) only considered vegetables in the study near a large-scale Pb/Zn smelter, and found that Pb and Cd pose greatest health risk and leafy vegetables tend to be more contaminated than non-leafy vegetables. Cereals were the only edible crops studied by Sharma et al. (2018), who found that maize grains act as hyper-accumulators of copper (BCF=30.43). Lu et al. (2018) only assessed the health risks of PTEs in rice, and found that Cd migrates more significantly and poses the greatest risk to human health. The study of Tl by Jia et al(2013) of the geochemical behavior of Tl at the interface of soil and green cabbage provided evidence of high accumulation of Tl, with most BCF values exceeding 1, and up to a maximum value of 11. More comprehensive studies including soil, drinking water and crops, conducted for example by Luo et al. (2019) found that the highest BCF values for Cd and Zn.

We report on a comprehensive study including leaf and root vegetables and cereals, which form the main dietary components in our study area. In addition, we include assessment for a wide range of PTEs, associated with the mining region. Typically As, Cd, Cr, cobalt (Co), Cu, Pb, Zn, Ni and mercury (Hg) which are the almost frequently assessed in mining and industrially contaminated soils and associated crop exposure human health risk assessments (Chen et al. 2018; Viraraghavan et al. 2011; Sharma et al. 2018; Lu et al. 2018; Lian et al. 2019). The inclusion of Tl in these assessments is extremely rare. Even though Tl is a highly toxic element, comparable to that of Cd, Hg and Pb (Peter et al. 2005; Viraraghavan et al. 2011), its general abundance is low and is not a common environmental pollutant unlike those highlighted above. Consequently there are few examples of field study data and little is known about its food chain transfer.

Thallium minerals are rare in nature, and Tl is generally found in soils with low concentrations (Xiao et al., 2004). For soils, TI is often excluded from the list of elements to be analyzed, as its concentration in uncontaminated soils range from 0.01 to 3 mg/kg, while most soils contain Tl at concentrations of less than 1 mg/kg (Fergusson, 1990). For plants, the average concentrations of Tl in the land plants reported by Bowen (1979) were 008-1.0 mg/kg and that in the edible plants were 0.03-0.3mg/kg, on dry weight basis. Thus, a better understanding of the local environmental impact of TI is essential to identify, seek remediation options and manage any Tl-related health issues. We report on an assessment of common food basket ingredients of the population lining in and around a Tl mining area. This included six common food crops (Chinese cabbage, cabbage, pepper, radish, chilli, corn and rice) for which the contents of Tl, As, Cd, Pb, Ni, Cu and Zn were determined and used in health risk assessment.

2. Materials and methods

2.1. Study area

The study area is located in a village in southwest Guizhou province, China (Jia et al. 2013). This area has an independent thallium deposit and coal mine, where arsenic ore is also concentrated. The mining history of the study area shows activity for more than 300 years (Xiao et al. 2003). Now the area has been widely developed for agriculture and residential land, the majority of residents have permanent dwellings and total about 1000 people. The climate of the study area is mild and humid, with an average temperature of 14°C, the annual precipitation is 1300 ~ 1500 mm, with the main rainy season in summer and autumn concentrated in July and August (Xiao et al. 2003). Investigations during fieldwork highlights that these residents predominantly use locally grown (personal and purchased from neighbors) staple foods and the economic development of the district is relatively poor. The main local food corps are: rice, corn, Chinese cabbage, green cabbage, chili and carrot. Cases of more than 400 people have been found to be poisoned by thallium in the study area since the 1960s, which highlights extensive pollution of the region (Jia et al. 2013).

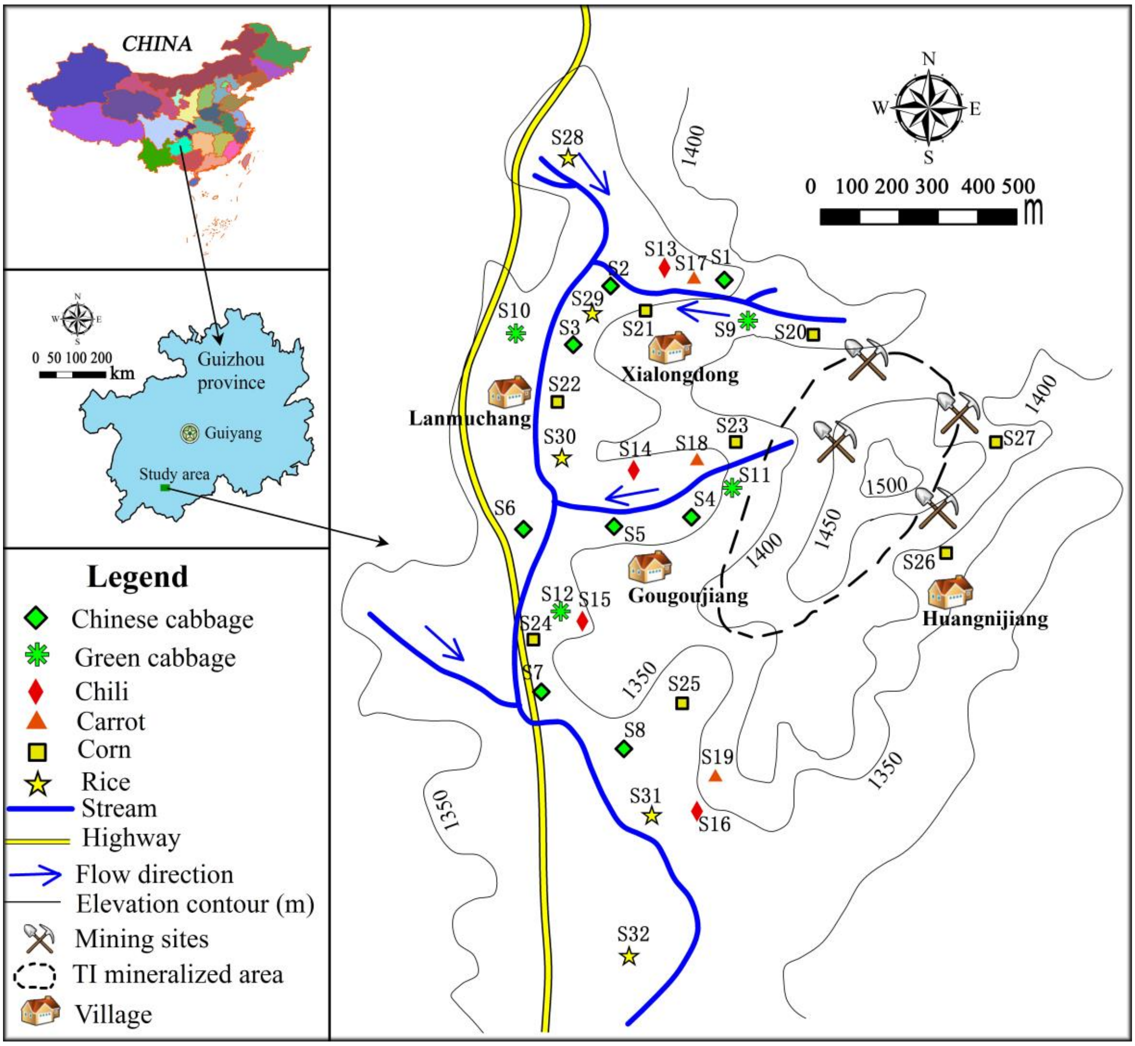

Figure 1. Sampling sites for six crop types in thallium mining area.

2.2. Sampling and analytical methods

2.2.1. Sampling methods and preparation

Six common food crop products, namely, Chinese cabbage, green cabbage, chili, carrot, corn and rice, were used as samples of food exposure (Figure 1). In order to ensure representative sampling, we randomly selected the edible parts of many plants at each sampling point, and combined to make a composite sample. Each crop was collected at its most mature/ripe stage (within the same season/in the year 2018). The edible parts of the crops were carefully cleaned of attached soil and washed with deionized water, then the surface moisture was dried with filter paper, and dried in the oven for one hour (100 °C). Finally, drying to constant weight at 60 °C. The dried crops are ground into fine powder and pass 100 mesh nylon sieve, then stored in sealed polyethylene bags at 4 °C.

Soil samples were collected at the crop sampling site at the same time. Sampling was to a depth of 0~ 20cm (equivalent to general depth of crop roots in the soil), stored in polyethylene bags, and then transported back to the laboratory. Soil samples dried naturally in air and obvious impurities removed, then ground into fine powder and pass 100 mesh nylon sieve, stored in sealed polyethylene bags at 4 °C.

2.2.2. Analytical methods

The analytes: Tl, As, Cd, Pb, Ni, Cu and Zn were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, JY38S, Jobin Yvon, Longumeau, France). Analytical duplicates, reagent blank, national standard soil sample (GBW07401) and plant sample (GBW07602) were used for quality control during instrument testing. Crop samples were digested using HNO_3 and H_2O_2, Soil samples were digested with aqua regia. Concentrations of PTEs in soil and crop digestion solution were determined by ICP-AES. The determination procedure is as described in our previous reports (Jiang et al. 2019). Average recoveries for PTEs plant and soil reference materials were 94.8% to 106.5% (RSD: 0.18%–3.72%), respectively.

2.3. Contamination assessment of crops

The single factor pollution index can evaluate the pollution degree of a single PTE in crops, and the comprehensive pollution index can evaluate the comprehensive pollution level of all pollutants in each crop (Li et al. 2018). The two indices can be used together and are considered to be a comprehensive and practical method in the assessment of plants contamination levels (Li et al. 2018; Yang et al. 2008), and are shown in Eqs. (1) and (2):

$$P_i = C_i/S_i \quad (1)$$

Where P_i is the single factor pollution index of pollutants in a crop; C_i is the measured value of pollutants in a crop (mg/kg, FW) on fresh weigh basis; S_i is the assessment standard for pollutants, usually the maximum allowable concentration. We used the maximum allowable concentration as an appropriate level for the population being studied due to high localized contamination. Our concern was to use data relvant to local population and then any standards provided by other organizations. The regulated pollution level of China is applied for S_i for the criteria, with GB 2762-2017 for As, Cd and Pb , GB 15199-94 for Cu and GB 13106-91 for Zn on a fresh weight basis. At present, China only sets nickel limits for margarine and other oils, but not for other foods, so we obtained the limited level of Ni in crops from FAO/WHO on a fresh weight basis (FAO/WHO, 2011). Because the concentration of thallium is very low in nature, there is no specific food limit standard for thallium at present so we set the limit level for Tl in food crops as 0.3 mg/kg on the basis of dry weight (Bowen, 1979) (more details provided in Table 2).

$$P = \sqrt{\frac{\overline{P}_{\mathrm{i}}^{2} + P_{\mathrm{imax}}^{2}}{2}} \quad (2)$$

Where P is the comprehensive pollution index, $\overline{P}_{\mathrm{i}}$ is the average of the single-factor pollution index, and P_{imax} is the maximum of the single-factor pollution index.

The evaluation of single factor pollution index and comprehensive pollution index can be classified into five grades: Class I, P≤0.7 is safe; Class II, 0.7＜P≤1 is clean; Class III, 1＜P≤2 is slightly polluted; Class IV, 2＜P≤3 is moderately polluted; Class V, P＞3 is heavily polluted.

2.4. Bioconcentration factor

The crop bioconcentration factor (BCF) is the ratio of the content of the element in the plant to the content of the element in the soil of the corresponding cultivated soil. The BCF is a parameter that characterizes the effect of soil element content on food chain. It is dimensionless and so objectively reflects the potential of plant to accumulate trace elements from soil. The higher the BCF value is, the stronger the ability of the plant to accumulate the element and the weaker its ability to act as a barrier to soil metal pollution. Where BCF > 1 it indicates that the plant is a net accumulator of the element (Yang et al. 2008). The bioconcentration factor (BCF) was calculated using by the following equation:

$$BCF = \frac{C_{plant}}{C_{soil}} \qquad （3）$$

Where C_{plant} and C_{soil} are the concentrations of PTEs in crops (based on dry weight) and soil (based on dry weight) sampled from the same site, respectively (Lian et al. 2019).

2.5. Health risk assessment

The target hazard quotient (THQ) and hazard index (HI) were used to assess the potential health risks of exposure to PTEs through consumption of crops. THQ is the ratio of PTE exposure dose to reference dose. If THQ > 1, it indicates that the PTE has potential health risks to the exposed population, and the calculation is as follows (USEPA 1989):

$$THQ = \frac{C \times CF \times \mathrm{IR} \times EF \times ED}{BW \times AT \times \mathrm{RfD}} \qquad （4）$$

Where C is the concentration of PTEs in edible parts of food crop (on dry weight basis, mg / kg). The CF is the conversion factor from fresh to dry weight was 0.085 (Rattan et al. 2005); IR is consumption rate of a food crop, (kg / person / day; FW); EF is exposure frequency (365day/year); ED is exposure period (70year); BW is the body weight, and the average BW for adult is set to 60kg; AT is the average exposure time (ED*365day/year); RfD is the daily oral reference dose, RfD for Tl, As, Cd, Pb, Ni, Cu, Zn are 0.00008, 0.0003, 0.001, 0.0035, 0.02, 0.04, 0.3 mg/kg/day, respectively (IRIS 2003; USEPA 2009). The average daily consumption of Chinese cabbage, carrots, green cabbage, chili, corn and rice were 0.08, 0.041, 0.029, 0.015, 0.002, 0.25 kg / person / day for adults, on fresh weight basis (Zhao et al. 2016; Hulshof 1998).

The Hazard Index (HI) indicates that the total risk of all PTEs in food crops (USEPA 1989). If HI ≤ 1, there was no significant negative effect; HI > 1, indicating a high probability of negative effects on human health; and HI > 10, indicating a chronic toxic effect.

$$HI = \sum_{n=1}^{t} THQ_n ; \quad t=1,2,3 \ldots n \qquad (5)$$

Where n is the nth PTE. In this study, HI is the sum of THQ of Tl, As, Cd, Pb, Ni, Cu and Zn.

3. Results and discussion

3.1 PTE in farmland soils and food crops

There are two main reasons for the excess of PTE in crop: the content of PTE in farmland soil is too high, or the crops have a good ability to absorb one or several elements from the soil. Therefore, the information of PTEs content in farmland soil can help better understand of the cause of the contamination of edible crops. The concentrations for PTE in farmland soil from the thallium mine area are presented in Table 1. The average concentrations of Tl, As, Cd, Pb, Ni, Cu, and Zn were 34.69 mg/kg, 156.95 mg/kg, 0.43 mg/kg, 35.00 mg/kg, 63.41 mg/kg, 87.00 mg/kg, and 95.34 mg/kg, respectively; corresponding to 48.72, 7.84, 0.65, 0.99, 1.62, 2.72, and 0.96 times the background values of soil in Guizhou Province. It indicates that the Tl in the farmland soil seriously exceeds the environmental standard, with As. Ni and Cu more than two times the standard. Distribution, source identification and detailed contamination status of PTE in the soil of the study area can be seen from our previous reports (Jiang et al. 2019).

Table 1 Descriptive statistics for PTEs contamination status of the farmland soil (mg/kg).

Element	Min	Max	Mean±S.D	B V	B V±S.D
Tl	14	124	54.69±24.37	0.712	0.712±0.293
As	106	404	206.00±82.58	20.0	20.0±14.55
Cd	0.20	0.80	0.43±0.14	0.659	0.659±1.406
Pb	15	95	35.00±18.07	35.2	35.2±19.59
Ni	27	125	63.41±22.08	39.1	39.1±22.4
Cu	31	127	87.00±25.66	32	32±20.76
Zn	29	146	95.34±28.18	99.5	99.5±56.01

Min = minimum; Max = maximum; CV = coefficient of variation; S.D = standard deviation.

BV=Background Values, According to the Background value of soil elements in China (China National Environmental Monitoring Centre, 1990)

The concentrations of PTEs and food standards for the edible parts of different crops in the study area are shown in Table 2. Except for the limit levels of As, Cd, Pb, Ni, Cu and Zn, the other listed concentrations are based on dry weight. The concentrations of Tl, As, Cd, Pb, Ni, Cu and Zn in the six crops ranged from 0.3~494.4 mg/kg, 0.01~1.39 mg/kg, 0.01~0.85mg/kg, 0.03~12.0 mg/kg, 0.1~18.4 mg/kg, 0.2~6035 mg/kg, 14~119 mg/kg, respectively with the concentration of PTEs in vegetables (Chinese cabbage, green cabbage, chili, carrot) being higher than that in grains (corn, rice). If data are presented on a fresh weight basis, the concentration of As, Cd and Pb are close to element limit levels for individual crops. Except for Cu in carrot, the concentrations of Ni, Cu and Zn in crops are very low. The concentration of Tl was relatively high in all crops, especially in green cabbage, it indicates that Tl is easily taken up by plants and Green cabbage act as hyper-accumulators of Cu, which has been identified by many studies (LaCoste et al. 2001; Xiao et al. 2004; Al-Najar et al. 2005; Pavlickova et al. 2005; Jia et al. 2013). Thus, it is not surprising that the concentration of Tl in Green cabbage is very high in this study, due to the dual factors of elevated Tl in the soils and the super-accumulation property of Green cabbage.

Of the seven PTEs, Tl is highlighted as the main pollutant in crops, and the average concentration of Tl in all crops is significantly higher than the relevant standard. Compared with the previous reports of PTEs (especially Tl) in vegetables and crops in this area by Prof. XIAO Tangfu's group, the content of PTEs in many crops is very similar or slightly (but not significantly) lower. It can be inferred that the concentration of PTEs in crops is species-specific and there is variation with the concentration of PTEs in soil where the crops grow. The content of PTEs in farmland soil will migrate to crops, which will lead to the decrease of PTEs in soil and crops year by year. However, for strongly accumulating crops depletion of PTEs in soil by crop growth is too low to achieve sanitation of heavily polluted sites (sager, 1988). On the other hand, PTEs in the farmland soil are influenced by agricultural activities which include the addition of wastewater sludge and cinders from local residents as soil improvers, in addition to inputs from continued mining activities (Jiang et al. 2019). Therefore, a number of factors may have led to changes in uptake of PTEs over time.

Previous studies have shown that plants with thick roots and strong active transport ability can absorb more PTEs from the soil (Shahid et al. 2016; Bondada et al. 2004). In this study, the crops with the highest As, Cd, Ni, Cu and Zn contents is carrot, which is consistent with other research (Shahid et al. 2016; Bondada et al. 2004). In addition to the absorption of PTEs by the root system (from the soil), the absorption of the leaves (from the atmosphere) is also the main way to transfer PTEs to crops (Shahid et al. 2016). This means that Chinese cabbage, green cabbage, chili and carrot are likely to be the more significant accumulators than cereals.

Therefore compared with other crops, the very high concentration of Cu in carrot and Tl in green cabbage is not surprising but also it can be clearly seen that the uptake of PTEs by crops varies both with the PTEs and crop types, due to the different physiological and absorption mechanisms.

Table 2. Concentrations of PTE in various crop (DW, mg/kg except where indicated).

Sample	Statistics	Tl	As	Cd	Pb	Ni	Cu	Zn
Chinese cabbage (n=8)	Mean±SD	2.1±2.0	0.76±0.31	0.27±0.10	3.1±3.7	2.1±0.7	6.0±1.6	54±19
	Min	0.7	0.17	0.15	0.4	1.0	3.5	30
	Max	5.4	1.25	0.43	12.0	3.3	9.2	92
	Limit level	0.3	0.5	0.2	0.3	67	10	20
Green cabbage (n=4)	Mean±SD	261±221	0.77±0.27	0.30±0.09	0.7±0.2	1.9±1.1	3.1±0.5	51±28
	Min	31.7	0.38	0.17	0.5	0.6	2.7	32
	Max	494.4	0.98	0.38	1.0	2.7	3.8	92
	Limit level	0.3	0.5	0.2	0.3	67	10	20
Chili (n=4)	Mean±SD	3.9±1.0	0.25±0.03	0.06±0.03	0.22±0.03	1.9±0.5	8.0±0.7	18±3.5
	Min	2.9	0.22	0.04	0.18	1.2	7.1	14
	Max	5.3	0.29	0.10	0.25	2.5	8.6	21
	Limit level	0.3	0.5	0.05	0.1	67	10	20
Carrot (n=3)	Mean±SD	21.7±5.5	1.24±0.16	0.80±0.06	1.86±0.20	16.8±1.65	5275±695	113±6.5
	Min	16.3	1.07	0.73	1.64	15.1	4671	106
	Max	27.2	1.39	0.85	2.01	18.4	6035	119
	Limit level	0.3	0.5	0.1	0.1	67	10	20
Corn (n=8)	Mean±SD	1.5±0.9	0.02±0.004	0.04±0.06	0.05±0.03	0.22±0.08	1.7±0.7	19±2.3
	Min	0.78	0.01	0.01	0.03	0.1	1.4	17
	Max	3.08	0.03	0.16	0.11	0.4	3.1	23
	Limit level	0.3	0.5	0.1	0.2	67	10	20
Rice (n=5)	Mean±SD	2.0±1.9	0.16±0.41	0.02±0.01	0.05±0.01	0.12±0.05	0.74±0.54	18±3.7
	Min	0.3	0.10	0.01	0.03	0.1	0.2	14
	Max	5.2	0.21	0.03	0.06	0.2	1.6	24
	Limit level	0.3	0.2	0.2	0.2	67	10	50

Limit level of Tl was obtained from Bowen et al (Bowen, 1979); limit level of As, Cd and Pb were obtained from GB 2762-2017 (MHPRC, 2017); limit level of Cu obtained from GB 15199-94; limit level of Zn obtained from GB 13106-91; limit level of Ni was obtained from AO/WHO (FAO/WHO, 2011); concentrations of limit level in GB 2762-2017, GB 15199-94, GB 13106-91 and FAO/WHO are based on fresh weight.

3.2. Bioaccumulation of PTEs

The BCF values of PTEs in different crops are shown in Table 3. The BCF values for Cd and Zn is higher than that of other elements in most crops, following the order of Cd > Zn > Cu > Tl > Ni > Pb > As, confirming behavior of the elements seen elsewhere (Lu et al. 2018; Lian et al. 2019), which also indicates that Cd and Zn have high transfer from soils to food crops.

In general, the order of BCF in crops is: rhizome vegetables (carrot) > leafy vegetables (Chinese cabbage and green cabbage) > fruit vegetables (chili) > cereal (rice and corn). This is consistent with the results of Li et al. (2018). Li et al. (2018) and Lian et al. (2019) also indicates that the cause of this phenomenon is related to strong root absorption and atmospheric deposition (leaf absorption).

The bioaccumulation of Cu in carrot was very strong (BCF=83.744), followed by Cd (BCF=1.932) and Zn (BCF=0.977). The bioaccumulation of Tl in green cabbage Tl was very strong (BCF=4.994). The highest enrichment for Pb is found in Chinese cabbage (0.100).The different accumulation across elements and crop types is likely to be more strongly controlled by physiological requirements (Shahid et al. 2016).

In general, it is worth noting here that several crops have strong bio-enrichment capacity for Cu, Tl, Cd and Zn. Whilst Cd and Zn are well known to be more mobile in soil and it is not be surprising to see high BCFs. The strong bio-enrichment of Tl in Chinese cabbage has been discussed above. Previous studies have also reported high Cu uptake by crops. For example, Lian et al. (2019) reported that the concentration of Cu in roots is higher than other parts for most vegetables. The pollution pathways of PTEs to crops include root absorption (from farmland soil) and leaf absorption (from atmospheric deposition) (Shahid et al., 2016). Besides, crops with massive roots can absorb more PTEs from the soil (Shahid et al., 2016). Thus, the leaf of carrot can absorb more PTEs from the atmosphere due to the larger leaf surface; and the large root/tuber of carrots may absorb more PTEs from the soil. On the other hand, our previous work confirmed that soil Cu in the study area is only slightly polluted, and the waste gas and slag produced by coal combustion are the main sources of Cu pollution (Jiang et al. 2019). Thus, the high concentration of Cu and its BCF in carrots may be related to both soil absorption and atmospheric deposition, which is consistent with Li et al.(2018).

Table 3. Bio-concentration factors (BCF) for PTEs in different crops.

Crop	Tl	As	Cd	Pb	Ni	Cu	Zn
Chinese cabbage	0.048	0.005	0.661	0.100	0.034	0.070	0.542
Green cabbage	*4.994*	0.004	0.760	0.018	0.039	0.038	0.575
Chili	0.068	0.002	0.152	0.008	0.030	0.105	0.194
Carrot	0.366	0.006	*1.932*	0.062	0.397	*83.744*	0.977
Corn	0.028	0.001	0.101	0.002	0.004	0.029	0.253
Rice	0.048	0.001	0.056	0.002	0.002	0.007	0.284

3.3. Significance of Contamination of the edible crops

The contamination by Tl is very serious in all crops (Class V (heavily polluted)), especially in the case of green cabbage, (Table 4). The pollution indexes for As, Cd, Ni and Zn in very crops are low (all Class I (safe)). For As, Cd, Pb, Ni, Cu and Zn in cereals (corn and rice) classification is Class I (safe). The for Cu in carrot classification was very high (Class V: heavily polluted), followed by Pb (Class III: slightly polluted) The contamination level of As, Cd, Ni, Cu and Zn in Chinese cabbage, cabbage and chili showed Class I, the pollution index of were all less than 0.7 (safe) in these three vegetables. There is no Pb contamination in Chinese cabbage (Class II: clean), and in carrot was slightly polluted (Class III).

Except for the specific pollution in some crops, the order of degree of PTE contamination is Tl > Pb > As > Cd > Zn > Cu > Ni and for crops pollution follows: rhizome vegetable > leaf vegetable > fruit vegetable > cereal, as for the bioaccumulation factor for PTEs.

Table 4. Single-factor (Pi) and comprehensive pollution (Class) indices for the edible crops.

elements	Chinese cabbage (n=8)		Green cabbage (n=4)		Chili (n=4)		Carrot (n=3)		Corn (n=8)		Rice (n=5)	
	Pi	Class	Pi	Class	Pi	Class	Pi	Class	Pi	Class	Pi	Class
Tl	7.017	V	870.583	V	12.858	V	72.333	V	4.800	V	6.633	V
As	0.129	I	0.131	I	0.043	I	0.211	I	0.003	I	0.067	I
Cd	0.115	I	0.125	I	0.102	I	0.680	I	0.029	I	0.09	I
Pb	0.864	II	0.205	I	0.183	I	1.581	III	0.020	I	0.020	I
Ni	0.003	I	0.002	I	0.002	I	0.021	I	0.001	I	0.001	I
Cu	0.051	I	0.027	I	0.068	I	44.843	V	0.015	I	0.006	I
Zn	0.230	I	0.216	I	0.074	I	0.479	I	0.082	I	0.031	I
P*	5.033	V	624.855	V	9.191	V	52.567	V	3.430	V	4.739	V

P*: Comprehensive pollution index

Note: Class I, safe; Class II, clean; Class III, slightly polluted; Class IV, moderately polluted; Class V, heavily polluted.

According to the comprehensive pollution index (P), the rank order for crop pollution was Green cabbage > Carrot > Chili > Chinese cabbage > Rice > Corn,. In this sequence, the comprehensive pollution levels of the six crops all reached Class V (heavily polluted), and the pollution of Green cabbage is extremely serious.

3.4 Human health risk

The THQ values of each element studied and the HI values of each crop are shown in Table 5. The order of health hazards to human in most crops was Tl > As > Pb > Cd > Cu > Zn > Ni, which is similar to their single-factor pollution index (P_i) in crops. Therefore, the higher the pollution index of crops, the more adverse the trend will be to human health. Hazard index (HI) values for each crop are ordered as Tl > Cu > As > Pb > Cd > Zn > Ni. The THQ value of Tl in all crops except corn exceeded the safety threshold of 1.0, and long-term consumption of these crops would cause harm to the body. Only the THQ of Cu in carrot exceeded the safety threshold (1.0), and consumption of Cu from other crops does not pose a risk to humans. The majority of PTEs studied (As, Cd, Pb, Ni and Zn) do not pose significant risk of harm to humans in all crops (THQ ≤ 1). It can be seen that even if some elements exceed the standard in crops or polluted in crops (see Table 1, 4), they do not pose a health hazard (e.g., Pb in carrot). In addition, Excessive PTE in the soil does not pose a risk to human health due to its low bioenrichment capacity through the food chain exposure.(e.g., As and Ni).

Figure 2 and Table 5 confirm that the exposure to Tl in the crops is the most harmful (except for Cu in carrots). The order of decreasing HI was Green cabbage > Carrot > Rice > Chinese cabbage > Chili > Corn. Only corn demonstrated no negative effect on human health. Green cabbage was far more significant for human health than other crops, followed by carrot. The long-term consumption of rice, Chinese cabbage and chili is of concern from results here, while consumption of green cabbage and carrots will cause chronic toxic effects on human body (HI ＞20).

Table 5. THQ and HI values of PTE for local residents via crop consumption in the thallium mine area.

Crops	Target hazard quotient (THQ)							H I
	Tl	As	Cd	Pb	Ni	Cu	Zn	
Chinese cabbage	*2.982*	0.287	0.031	0.099	0.012	0.017	0.020	*3.448*
Green cabbage	*134.124*	0.011	0.012	0.009	0.004	0.003	0.007	*134.170*
Chili	*1.025*	0.018	0.001	0.001	0.002	0.004	0.001	*1.052*
Carrot	*15.755*	0.240	0.046	0.031	0.049	*7.661*	0.022	*23.804*
Corn	0.510	0.002	0.001	0.001	0.001	0.001	0.002	0.518
Rice	*8.810*	0.187	0.008	0.005	0.002	0.007	0.021	*9.040*
Total	*157.206*	0.745	0.099	0.146	0.070	7.693	0.073	

This study suggests that local residents may be over-exposed to Tl and Cu, through crops alone. However, exposure to PTEs through other exposure pathways such as drinking water, soil (ingestion, inhalation, and dermal contact) further increases the health risk from exposure to PTEs (Zheng et al. 2007; Järup 2003; Simsek et al. 2000). It is worth noting that although the degree of pollution and bioconcentration of rice is lower than that of Chinese cabbage and chili, the risk to human health is greater than that from consumption of Chinese cabbage and chili due to significance of rice in the daily diet of residents in the study area.

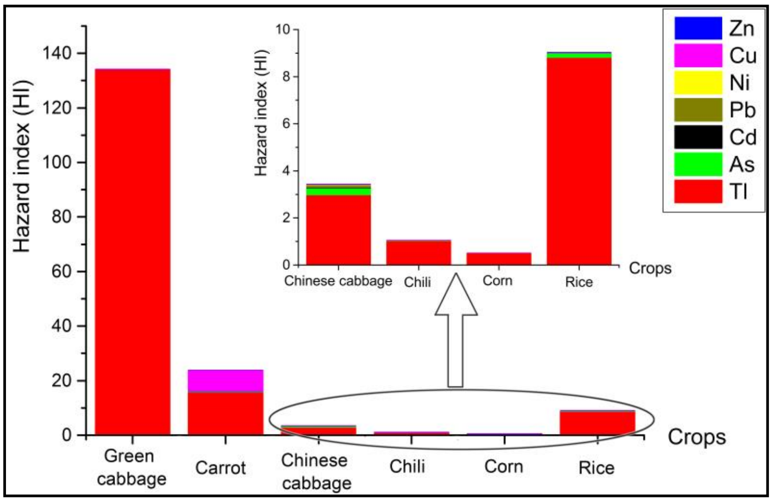

Fig. 2. Hazard index for consumption of subsistence crops grown in thallium mining area.

4. Conclusions

In this study, we compared the pollution status of a number of PTEs in crops from a thallium mining area, analyzed the absorption ability of PTEs in vegetables and cereals, and evaluated the health risks caused by eating these crops. It was found that Tl intake via consumption of all food crops posed high risk to human health from the study area as compared to other elements, due to its high toxicity and high concentration in crops. It was also found that Green cabbage was found to be hyper-accumulator of Tl, whereas, carrot acted as hyper-accumulator of Cu. This could be attributed to variable physiological requirements and uptake mechanisms of different crops and PTEs status in the environment. Moreover, the contamination of PTEs in crops, either through the uptake from root absorption (from farmland soil) or leaf absorption (from atmospheric deposition), poses a health concern to local residents. In addition, food crops should be avoided in the study area, and plants with high uptake of PTEs should be planted to reduce the concentration of PTEs (especially thallium) in food crops. We also highlight the need to use location specific data – particularly on consumption patterns to allow realistic risk analysis.

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