



Potentially toxic elements (PTEs) in crops, soil, and water near Xiangtan manganese mine, China: potential risk to health in the foodchain

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Abstract The pollution from large-scale manganese mining and associated industries in Xiangtan (south Central China) has created a significant burden on the local environment. The proximity of mining, and other industrial activity to the local population, is of concern and impact of past industrial on the food chain was evaluated by the assessment of common food groups (rice, soybean, and sweet potato), and the associated soil and water in the region. We focused on specific potentially toxic elements (PTEs): Mn, Pb, Cd, Cr, Cu, and Zn associated with industrial activity, identifying the distribution of pollution, the potential significance of total health index (THI) for local people and its spatial distribution. The study area showed severe contamination for Mn, followed by Cd and Pb, while

other PTEs showed relatively light levels of pollution. When analyzing the impact on crops exceeding the tolerance limit, the dominant PTEs were Mn, Cd, and Pb, with lower significance for Zn, Cu, and Cr. The average THI value for adults is 4.63, while for children, is 5.17, greatly exceeding the recommended limit ($HQ > 1$), confirming a significant health risk. In the spatial distribution of the THI, the region shows strong association with the transport and industrial processing infrastructure. Long-term management needs to consider remediation aligned to specific industrial operations and enhance contamination control measures of ongoing activity.

Keywords Manganese mining area · Potentially toxic elements · Health risk assessment · Spatial distribution · Total health risk

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Introduction

With the acceleration of the process of urbanization and industrialization and the rapid development of social economy, pollution by potentially toxic elements (PTEs) is an ongoing environmental hazard due to their persistence, toxicity and bioaccumulation potential (Xu et al. 2016; Liu et al. 2017; Chen et al. 2018). While many of these elements are essential for life in trace concentrations, they can enter the food chain through accumulation in crops or from exposure to associated soil and dust (Azhari et al. 2017; Chen et al. 2019). The effects from exposure to excessively high concentrations may lead to mental illnesses, e.g., Mn, and in more extreme situations cause of Parkinson's disease (Li et al. 2018) with the bioaccumulation of unwanted, hazardous elements indicated by obvious biomarkers, e.g., blood lead (Pareja-Carrera et al. 2014). Excessive intake of copper under industrial exposure can cause damage to the liver and central nervous system, and more serious can lead to depression and lung cancer (Sani et al. 2017).

The environmental impact of metal mining and processing is derived from the uncontrolled release of materials during processing, with large amount of tailings slag and smelting wastewater will lead to impact on the surrounding soil and water, which will eventually enter the human body and have a range of adverse effects (Jiang et al. 2018; Sun et al. 2018; Ren et al. 2015). The intensification of industrial activity and scale of exploitation has led to many mining areas and industrial regions being contaminated to such an extent that risk to human health is of concern (Braennvall et al. 2016; Liu et al. 2010). This is particularly true in rapidly developing economies where drive for mineral exploitation often outstrips implementation of robust exposure/release control measures (Entwistle et al. 2019). Although the health risks of many elements have been extensively studied (Liu et al. 2017; Cai et al. 2015; Chen et al. 2015; Ren et al. 2016), very little research is directed to the element manganese, and where it exists, is often on a limited exposure pathway (Huang et al. 2008; Mehmood et al. 2019). We used the opportunity from a regional manganese mining activity to consider human health risks with exposure mediated by three major dietary crops (rice, soybean, and sweet potato), associated soil and drinking water. This is extended to add a spatial assessment to derive the potential total

health risk (THI) using a sequence of bioaccumulation, pollution load, and individual risk indices (Chen et al. 2018; Huang et al. 2008; Lian et al. 2019; Wu et al. 2018).

Potential health risks from PTEs can be assessed by non-cancer risk assessment methods. We can use hazard quotient (HQ), hazard index (HI), and THI to assess non-cancer risk (Chen et al. 2018; Huang et al. 2008). These methods are often used to review the significance of pollution loading, and provide a useful method to scale and prioritize potential health risk (Zheng et al. 2007; Jiang et al. 2019). Below that the bio-concentration factor (BCF) is used to estimate the ability of elements to accumulation from soil to crops and highlight most significant components of local food basket and the single pollution index (P_i) can be used to indicate the extent of soil contamination for each metal. Given the operational activity at the mining site varied in intensity and specific process, the use of Kriging interpolation provides very important spatial feedback. The visual distribution of both primary inputs and derived health risk provides an opportunity to more intuitively analyze the data obtained. The feedback from assessment around Xiangtan Manganese Mine also provides guidance for local government on the implementation of environmental protection programs and serves as a template for risk assessment of other mining areas in China.

The main purposes of this study are: (1) Measure the concentration of heavy metals in crops (rice, soybean, and sweet potato), soil and drinking water around the Xiangtan manganese mining area. (2) Calculate the HQ of each PTE, the HI, and the THI value of the local people through the above five pathways. (3) Estimate the HQ, HI, and THI values of the entire study area, and analyze their spatial distribution by Kriging interpolation.

Materials and methods

Research area

The study area is located in a manganese mining area in Xiangtan City in the east central Hunan Province in south central China (between 28°0'0"N-28°5'0"N, and 112°48'30"E-112°55'0"E). Exploitation of Mn hosted in carbonate rocks and wider environmental impact

has been described previously (Jiang et al. 2018). The area under investigation is approximately 53.50 km². The study area has a subtropical monsoon climate, and the climate is characterized by mild climate and abundant precipitation, simultaneous rain and heat, and four distinct seasons (Fang et al. 2006). A short spring (March to April) and autumn (October to November) with longer summer (May to September) and winter (December to February) periods.

The annual average temperature in the study area is 17.2 °C, and the annual average rainfall is about 1300 mm, with the rainfall is mainly concentrated in the summer. The prevailing winds are mostly southerly in summer and the northwest winds in winter. Some heavy industrial enterprises in addition to direct mining, include smelting and chemical manufacturing industry, have evolved in the area as part of the industrial expansion of Xiangtan City, causing pollution of the surrounding environment (Jiang et al. 2018; Zhang et al. 2004).

Sample collection

We systematically selected the soil and the edible parts of rice, soybeans, and sweet potatoes in field from the study area, close to harvest time. A total of 45 sample points were selected at locations where crops could be sampled (15 rice samples, 15 soybean samples, and 15 sweet potato samples). A total of 55 soil samples were collected from surface (0–20 cm), with a 1000 g bulk sample composited from five subsamples separated by 5 m spacing in each field. A total of 15 rice soil samples, 15 soybean soils sample, 15 sweet potato soil samples, and ten non-agricultural soil samples were collected as shown in Fig. 1.

Samples were shipped to the laboratory immediately after collection. Crop samples were washed with deionized water before oven drying (65 °C) to constant weight and then ground to pass through a 250 µm sieve. The soil samples were naturally air dried on the bench and stone and plant roots were removed before passing through a 0.9 mm nylon screen. All samples were stored in polyethylene bags for further analysis (Li et al. 2012).

Water samples were from common drinking water points taken from a series of ten locations randomly selected across the study area. A series of 1L of drinking water was collected after running taps for 30 min to flush pipe work, into acid-washed

polyethylene plastic bottles and stored at 4 °C until analyzed.

Sample analysis

Soil sample analysis

Aliquots of soil (0.5 g) were digested with 15 mL of concentrated HNO₃-HF-HClO₄ in a Teflon beaker at 85 °C until a clear solution was obtained (Lian et al. 2019). Samples were filtered and diluted to 50 ml with water (deionized) for analysis. The concentration of Mn, Pb, Cd, Cr, Cu, and Zn in each solution was determined by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer SCIEX, Elan 9000).

Crop sample analysis

A series of 1.0 g sample aliquots were placed in a Teflon beaker and digested with 15 mL of concentrated HNO₃ + H₂SO₄ + HClO₄ (HNO₃:H₂SO₄:HClO₄ = 5:1:1) and the sample at 80 °C until a clear solution is obtained (Mehmood et al. 2019), filtered and diluted to 50 mL with deionized water. The concentration of Mn, Pb, Cd, Cr, Cu, and Zn in each solution was determined by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer SCIEX, Elan 9000).

Drinking water sample analysis

All filtered and acidified water samples were analyzed for target PTEs (Mn, Pb, Cd, Cr, Cu, and Zn) by using graphite furnace atomic absorption spectrometer (Perkin Elmer, AAS-PEA-700) under standard operating conditions.

Analytical Quality Control

In order to confirm the accuracy of sample analysis, standard natural matrix reference materials (China National Standards Research Center) were analyzed along with field samples. These included soil (GBW07405); plant (GBW07602); and water (GBW(E)080194). The recovery rates of the target PTEs in the standard references ranged from 95% to 105%. In all analytical procedures, each sampling point (soil, food, water) was analyzed in triplicate, and

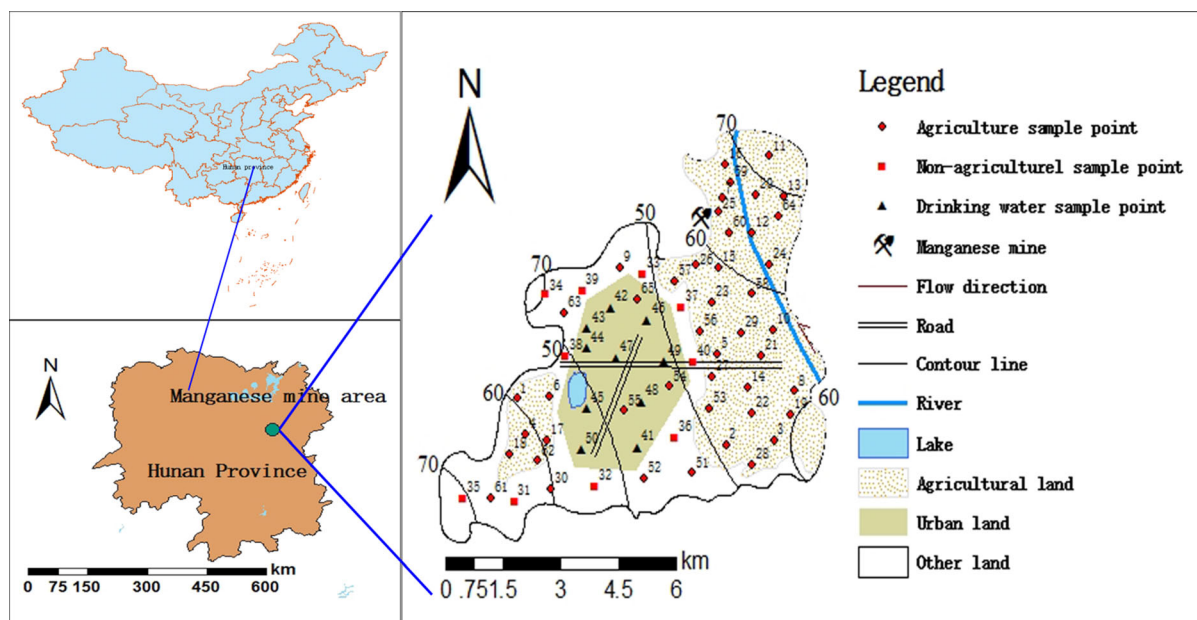


Fig. 1 Simplified map of study area and sampling points

method blanks were included to check for contamination.

Data analysis

Bio-concentration factor (BCF)

BCF is the ability to transfer PTEs from the soil to the edible portion of the crop. BCF of six metals of Mn, Pb, Cd, Cr, Cu, and Zn can be calculated by the following equation (Cai et al. 2015).

$$BCF = \frac{C_p}{C_s}$$

where C_p and C_s represents the concentration of the element in crops and associated soil on a dry weight basis, respectively.

Single and comprehensive pollution indices

P_i is the ratio of the concentration of PTEs in contaminated soil to the concentration of PTEs in the reference soil and can be used to indicate the extent of soil contamination for each metal. The following equation can be used to calculate P_i (Yujun et al. 2011).

$$P_i = \frac{C_s(\text{Sample})}{C_r(\text{Reference})}$$

where C_s (Sample) represents the elemental concentration in contaminated soil; C_r (Reference) represents the background value of metal in soil in Hunan Province, respectively.

The soil pollution caused by multiple PTEs can be expressed by the Nemeru comprehensive pollution index (P_c). P_c not only considers the average pollution of each PTE, but also highlights the element contributing the most to soil pollution. The following equation can be used to calculate P_c (Zhang et al. 2011; Broeg and Lehtonen 2006).

$$P_c = \sqrt{\frac{[\max(P_i)]^2 + (\frac{1}{n} \sum_{i=1}^n P_i)^2}{2}}$$

where P_i represents a single pollution index for each PTE.

Risk from each PTE

HQ indicates the potential risk from each PTE. The calculation of HQ uses the ratio of the estimated value of contaminants ingested by consumption of contaminated crops, soil, and water to the local reference dose (RfDo) (USEPA 2005).

$$HQ = \frac{CDI}{RfDo}$$

$$CDI = \sum_{i=1}^n \frac{C_i \times IR_i \times EF_i \times ED_i}{BW \times AT_i}$$

where CDI represents “chronic daily intake,” which means the mass of the substance contacted per unit bodyweight per unit time (USEPA 1992). The RfDo represents an estimate of the daily exposure of the population to contaminated materials. The RfDo for the six metals of Mn, Pb, Cd, Cr, Cu, and Zn are 0.14; 3.6×10^{-2} ; 5.0×10^{-4} ; 1.5; 3.7×10^{-2} ; 0.3 mg/kg/day, respectively (USEPA 2000). The value for C_i is the concentration of PTE (mg/kg) in the exposed medium i . IR_i is the daily consumption rate (kg/person/day) of exposure medium i with the average daily consumption rate in the study area is: rice: 216.7 g/day for adult and 98.3 g/day for children, soybean: 75.5 g/day for adult and 37.4 g/day for children, sweet potato: 156.1 g/day for adult and 68.4 g/day for children, and water: 1.73 L/day for adult and 0.94 L/day for children. While IR_i for soil is based on the US Environmental Protection Agency’s regulations: 64 mg/day for adult and 104 mg/day for children (USEPA 2000). EF_i is the exposure frequency (365 day/year). ED_i is the exposure duration (65 years for adults and eight years for children were assumed in this study). BW (kg/person) is the average weight of people in the study area (65.4 kg for adult and 26.8 kg for children). AT_i is the average exposure time for the non-carcinogenic risk ($AT_i = ED_i \times 365$ day/year) (Chen et al. 2018). When the $HQ < 1$, it is considered that such a metal has no harmful effect on humans. Conversely, when the $HQ > 1$, it is considered that there may be a health risk, and as the HQ value increased, the health risk increases (Cao et al. 2014).

HI of multiple PTEs

The HI is used to assess the overall potential risk of multiple PTEs. HI is based on the EPA Chemical Mixture Health Risk Assessment Guidelines.

$$HI = \sum HQ$$

THI via the five pathways

The THI is equal to the sum of the HI values for each exposure route. For this study, THI refers to the value for humans through the intake of contaminated crops (rice, soybeans, and sweet potatoes), soil, and water.

$$THI = \sum HI$$

Results and discussion

PTE concentration data

PTE levels in soil

Box plots summarizing the concentration data for PTEs in the different soil samples in the study area are shown in Fig. 2. The order of magnitude of average concentration of the PTEs in the four soils varies between elements; however, Mn = non-agricultural soil (NS) > rice soil (RS) > soybean soil (SS) > sweet potato soil (PS), Pb = RS > PS > SS > NS, Cd = NS > SS > RS > PS, Cr = NS > PS > SS > RS, Cu = NS > SS > PS > RS, Zn = NS > RS > PS > SS. However, a general trend is that the non-agricultural soils seems to be more polluted than the agricultural soils across the study area, which may reflect the impact of agricultural practice turning over surface soils and diluting with less contaminated material from deeper in the profile.

The Mn concentration exceeded all of its background values in all four soils with Cr all concentrations lower than soil background value. The percentage concentration in RS, SS, PS, and NS exceeding background values were 86.7%, 73.3%, 86.7%, and 90%, respectively, for Pb, 60%, 66.7%, 53.3%, and 100% for Cd, 20%, 33.3%, 33.3%, and 80% for Cu, 60%, 26.7%, 20%, and 80% for Zn. These results indicate that the PTE content in the soil of the study area is significantly higher than its corresponding soil background value (CEME 1990) confirming, as anticipated, significant accumulation of PTEs in the study area. Of the six PTEs, Mn, Pb, and Cd were most significant.

P_i and P_c for the study area is shown in Figure S1. The P_i of Mn in soil is the highest, while the lowest for Cr (< 1). The P_i of other PTEs range from 1 to 2,

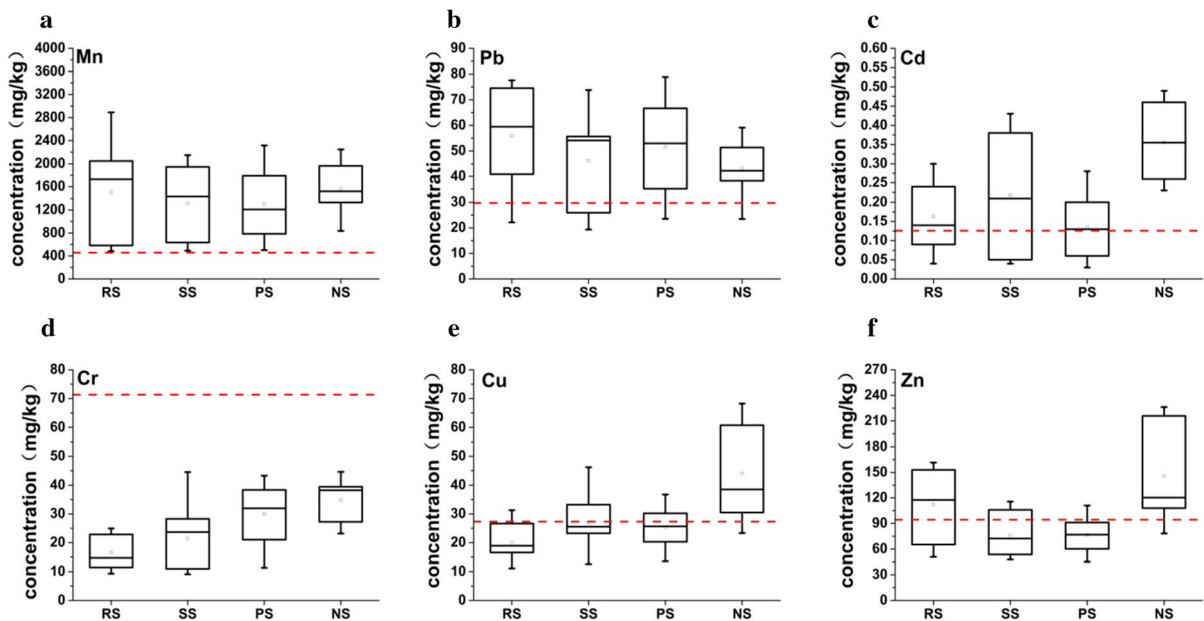


Fig. 2 Concentration diagram of six PTEs in four soils, and red dotted line indicates its soil background value (China Environmental Monitoring Center 1990)

showing that the soil in this study area is generally heavily contaminated by Mn, while for other elements the contamination is relatively light. The comprehensive pollution index in rice soil, soybean soil, sweet potato soil, and non-agriculture soil was 2.46, 1.97, 2.21, and 2.75, underlining trends indicated in individual element contamination.

PTE concentration in crops

The concentration of PTEs in crops is shown in Fig. 3. The order of average concentration of the six PTEs was Mn > Zn > Cu > Pb > Cr > Cd for rice, soybean, and sweet potato, respectively. The order of average value of BCF in the three crops is Cd > Zn > Cu > Mn > Cr > Pb, which is consistent with the previous studies (Zhang et al. 2018).

The concentration range (average) for manganese in the different foods was as follows: rice 15.29 to 96.16 mg/kg (50.13 mg/kg), soybean 13.48 to 66.64 mg/kg (41.39 mg/kg), and sweet potato 18.17 to 78.64 mg/kg (48.67 mg/kg) (Fig. 3). The order of the average concentration of Mn in three crops was rice > sweet potato > soybean, and BCF was sweet potato > rice > soybean.

The element Pb is highly toxic to humans. In this study, the Pb concentration exceeded the limit in all the crop samples for rice and soybean, while 66.7% of the samples of sweet potato. The order of Pb concentration in the three crops was rice > soybean > sweet potato, and BCF was similar among the three crops and consistent with the previous studies (Chen et al. 2018).

For Cd concentrations: rice 0.03 to 0.14 mg/kg (0.09 mg/kg), soybean 0.02 to 0.10 mg/kg (0.06 mg/kg), and sweet potato 0.02 to 0.12 mg/kg (0.07 mg/kg) (Fig. 3). However, the limits for Cd in rice, soybeans, and sweet potatoes are different, with a limit of 0.20 mg/kg for rice and sweet potato and 0.10 mg/kg for soybean (Ministry Of Health 2012; Ministry of Agriculture 2004) and the average concentration of Cd is not greater than its limit in all three crops. However, the order of BCF for Cd is rice > sweet potato > soybean. This highlights the sensitivity of rice food pathway to any changes in Cd content in the environment. Cd is recognized as a very toxic substance for human health. The harm of Cd to the human body includes its own high toxicity and its ability to migrate from soil to crops. Compared with the previous studies (Huang et al. 2008), the BCF for Cd is higher,

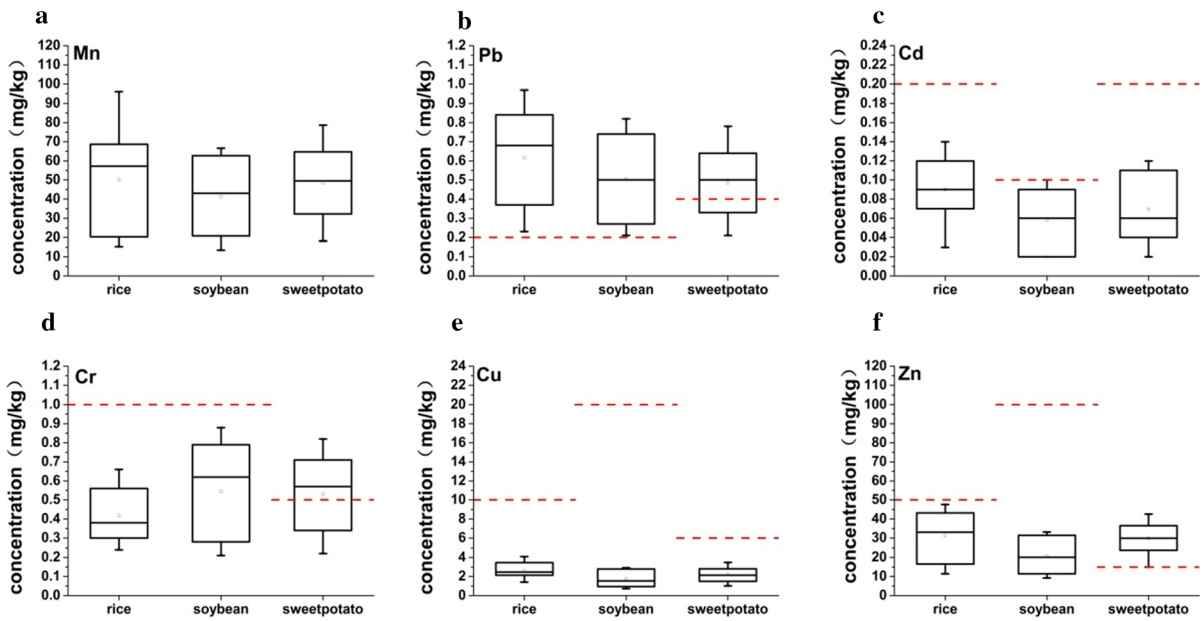


Fig. 3 Concentration diagram of six PTEs in rice, soybeans, and sweet potatoes, and dashed line indicates National food safety standards (see text). The red dotted line in the figure indicates the limits of different PTEs in crops for Pb, Cd, and Cr (rice and soybeans) from the National Food Safety

Standards for Food Contaminants (Ministry Of Health 2012) (GB2762-2012) and for copper, zinc (sweet potatoes) limit of eight elements in cereals, legume, tubers and its products (Ministry of Agriculture 2004) (NY861-2004)

indicating that there is more serious Cd pollution in this study area.

The concentration of Cr in all samples is less than its food standard limit for rice and soybean, while 60% of the sample points in the sweet potato sample point exceeded the limit with the. The order of the average concentration of Cr in the three crops is soybean > sweet potato > rice.

Like Mn, Cu and Zn are essential trace elements for the human body, and the concentration in three crops is relatively high (Vatansever et al. 2017). But for Cu in all samples, it is less than the regulatory limit. The average concentration for Cu is rice > sweet potato > soybean, and for BCF, rice > sweet potato > soybean.

The average concentration of Zn is less than the limit in rice and soybean, and greater than its limit in sweet potato with 93.3% of the samples exceeding food safety standards and follow the order: rice > sweet potato > soybean. The limit for Zn in sweet potato is very low compared to that for rice and soybean. The order of BCF is sweet potato > rice > soybean, highlighting the sensitivity of this food to contamination (Table 1).

PTE concentration in drinking water

The PTE concentrations in the drinking water at each site are listed in Table S1 of supplementary materials. All values for drinking water samples are less than the limits specified in the Sanitary standard for drinking

Table 1 BCF of six PTEs in rice, soybean, and sweet potato

	Mn	Pb	Cd	Cr	Cu	Zn
Rice	0.033 ± 0.0007	0.011 ± 0.0013	0.615 ± 0.1328	0.025 ± 0.0008	0.130 ± 0.0016	0.275 ± 0.023
Corn	0.031 ± 0.0016	0.011 ± 0.0015	0.314 ± 0.0833	0.026 ± 0.0041	0.063 ± 0.0239	0.260 ± 0.0453
Sweet Potato	0.038 ± 0.0035	0.009 ± 0.0003	0.548 ± 0.0820	0.018 ± 0.0014	0.085 ± 0.0074	0.389 ± 0.0474

water (Ministry of Health 2006)(GB5749-2006). Water consumption is not a significant source of PTE intake to the human body.

Health risk assessment

Average of HQ for each PTE

Since the drinking water in this study area was found to be below drinking water standard data were not used in subsequent calculations. The average value of HQ for each PTE after ingesting rice, soybean, sweet potato, and soil is shown in Table 2. The HQ value of each metal through four exposure pathways is greater in children than in adults, and the order of the HQ values is rice > sweet potato > soybean > soil. The dominance of rice as the main exposure route follows other work in similar contamination scenarios, with children highlighted as the most sensitive (Zheng et al. 2007; Fang et al. 2019; Kawser et al. 2015). The low HQ for the soil pathway reflects low transport risk, but the extent of contamination will influence crop content, so still forms a major component of the exposure scenario.

The average value of HI of multiple PTEs and its spatial distribution

Through consumption of crops from the area, contamination exposure for adults and children resulted in the HI values for the six PTEs in this study area: rice 2.42 (A) and 2.68 (C); sweet potato 1.57 (A) and 1.68 (C); and soybean 0.63 (A) and 0.76 (C) (Table 2). Rice again is highlighted as the most significant food source exposure route. For soil, the average HI value for children is approximately four times that for adults and should be considered in future exposure reduction/management (Cai et al. 2019). Given the relative concentrations and accumulation factors, the HI values are dominated by contributions from Mn, Cd, Zn, and Cu followed by Pb, and finally Cr.

The spatial distribution of HI values through the four significant exposure routes is shown in Fig. 4. The plots emphasize that the higher risk areas for crop exposure is generally in the southeast for soybean, for sweet potato and rice the northeast. For the soil pathway, the northern part of the area is higher risk, and does not overlap significantly with any of the crop exposure routes.

Table 2 Average of HQ, HI, THI for PTEs in adults and children

	Mn A(C) ^a	Pb A(C)	Cd A(C)	Cr A(C)	Cu A(C)	Zn A(C)	HI _i A(C)
HQ _{rice}	1.19 × 10 ⁰ (1.31 × 10 ⁰)	5.67 × 10 ⁻² (6.28 × 10 ⁻²)	5.96 × 10 ⁻¹ (6.60 × 10 ⁻¹)	9.25 × 10 ⁻⁴ (1.02 × 10 ⁻³)	2.34 × 10 ⁻¹ (2.59 × 10 ⁻¹)	3.47 × 10 ⁻¹ (3.84 × 10 ⁻¹)	2.42 × 10 ⁰ (2.68 × 10 ⁰)
HQ _{soybean}	3.41 × 10 ⁻¹ (4.13 × 10 ⁻¹)	1.62 × 10 ⁻² (1.96 × 10 ⁻²)	1.34 × 10 ⁻¹ (1.62 × 10 ⁻¹)	4.19 × 10 ⁻⁴ (5.06 × 10 ⁻⁴)	5.04 × 10 ⁻² (6.53 × 10 ⁻²)	7.93 × 10 ⁻² (9.59 × 10 ⁻²)	6.25 × 10 ⁻¹ (7.56 × 10 ⁻¹)
HQ _{sweetpotato}	8.30 × 10 ⁻¹ (8.87 × 10 ⁻¹)	3.23 × 10 ⁻² (3.45 × 10 ⁻²)	3.31 × 10 ⁻¹ (3.54 × 10 ⁻¹)	8.47 × 10 ⁻⁴ (9.05 × 10 ⁻⁴)	1.41 × 10 ⁻¹ (1.51 × 10 ⁻¹)	2.37 × 10 ⁻¹ (2.54 × 10 ⁻¹)	1.57 × 10 ⁰ (1.68 × 10 ⁰)
HQ _{soil}	1.09 × 10 ⁻² (4.33 × 10 ⁻²)	1.18 × 10 ⁻³ (4.66 × 10 ⁻³)	6.95 × 10 ⁻⁴ (2.76 × 10 ⁻³)	2.27 × 10 ⁻⁵ (9.01 × 10 ⁻⁵)	1.17 × 10 ⁻³ (4.62 × 10 ⁻³)	4.76 × 10 ⁻⁴ (1.89 × 10 ⁻³)	1.44 × 10 ⁻² (5.73 × 10 ⁻²)
THI							4.63 × 10 ⁰ (5.17 × 10 ⁰)

a: A(C)adult(children)

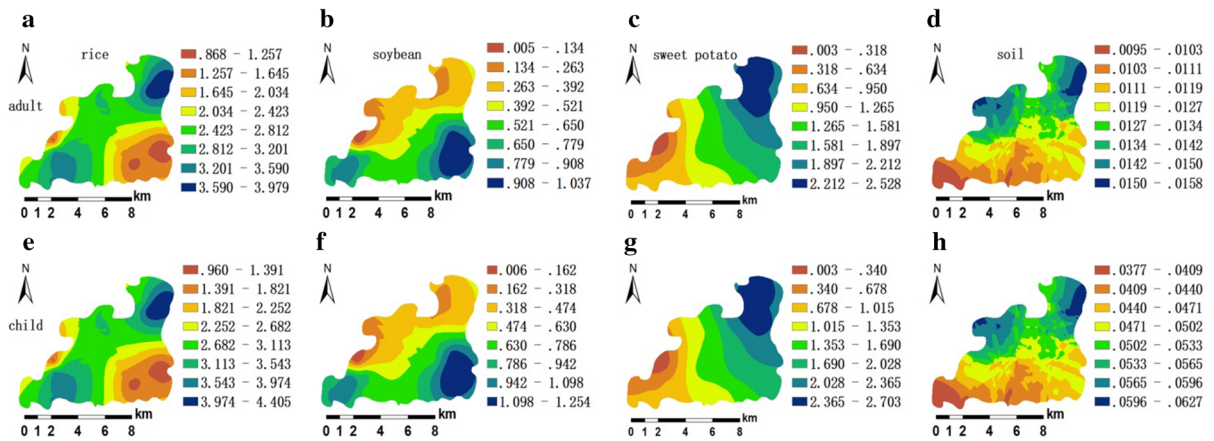


Fig. 4 HI diagram of four pathways for adults and children in Xiangtan Manganese Mine Area

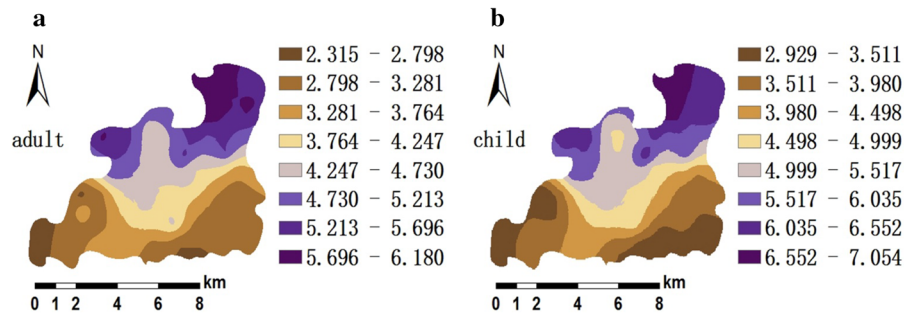


Fig. 5 THI values for Xiangtan manganese mines for adults and children

Average and spatial distribution of THI

The calculation of the average THI values of multiple PTEs by ingesting rice, soybean, sweet potato, and soil is shown in Table 2, and the THI values for adult and children in this study area were 4.63 and 5.17, respectively. This is much greater than 1 and indicates that local people may be exposed to serious health risks and that exposure is spatially very variable. Our THI value does not include, and special population groups more susceptible to pollution through work, lifestyle activity or underlying health conditions (Hang et al. 2009). The THI values was higher for children than adult, indicating that children were more vulnerable. The major contribution to the THI value was from rice consumption accounting for approximately 52.03% of the THI (with soybean 14.05%, and sweet potato 33%).

The spatial distribution of THI values for adults and children is shown in Fig. 5, and the northeast of the study area is highlighted as of particular concern. The

wide range of industrial activities in the Xiangtan City area includes smelters, chemical plants, and steel mills. These produce wastewater which discharged into local rivers. Much of this activity is concentrated in the northeast near the mining area, and transportation between the factory and the mine section further aggravates the pollution in the study area. For example, the combustion of leaded gasoline is a source of lead; Even though the utilization of leaded gasoline has been banned in China since 2000, elevated Pb contents in soils along the roadside were still widely reported recently (Yan et al. 2018). The low THI value located in the central zone of the study area reflects limited industrial development and more pristine countryside.

Uncertainty and limitations of risk assessment approach

In this study, the food consumption pathways from local staple crops such as rice, soybean, and sweet

potato and associated soil and drinking water were selected. The use of total concentrations to calculate health risks, an approach is still widely reported (Chen et al. 2018; Shaheen et al. 2016), but one that can introduce limitation to absolute risk assessment as the PTE exposure from these four pathways does not account for differences in absorption/availability of individual element. In addition, differences in consumption patterns were not fully assessed and may even enhance risk (Luo et al. 2012; Li et al. 2013). However, the spatial presentation of data highlights the significant divergence between risks from individual exposure routes and the potential value of this knowledge in preparing management plans for the region. Although there are so many limitations and uncertainties, our research is still very meaningful for the health risk assessment of the local population. Because it responded to the worst case, he provided the basis for the implementation of some local prevention policies.

Conclusion

This study assessed the contamination of rice, soybeans, sweet potatoes, soil, and water in the study area. Mn is the most polluted in the study area followed by Cd and Pb, while Zn, Cu, and Cr are less polluted. The comprehensive pollution index in RS, SS, PS, and NS of the study area was 2.46, 1.97, 2.21, and 2.75, respectively. It indicates that the pollution situation in the study area may have an impact on agricultural production and human health. Among the three crops in the study area, PTEs such as Mn, Cd, Pb, and Zn were more seriously polluted, while Cu and Cr were less polluted. For the study area, drinking water as a whole is safe for local people and does not pose a threat to their health.

The average of the THI values of multiple PTEs was obtained by ingesting four routes of rice, soybean, sweet potato, and soil. The THI values for adult and children in this study area were 4.63 and 5.17, respectively. It indicates that local people may be exposed to serious health risks and that children are exposed to health risks more severe than adults. In the study area, the THI value has a higher value for the northeastern part of the spatial distribution of the different exposure pathways, while the southwestern value is lower.

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References

- Braennvall, M. L., Bindler, R., Renberg, I., Emteryd, O., Bartnicki, J., & Billström, K. (2016). The Medieval Metal Industry Was the Cradle of Modern Large-Scale Atmospheric Lead Pollution in Northern Europe. *Environ.sci.technol.*, 33(24), 4391–4395.
- Broeg, K., & Lehtonen, K. K. (2006). Indices for the assessment of environmental pollution of the Baltic Sea coasts: Integrated assessment of a multi-biomarker approach. *Marine Pollution Bulletin*, 53(8), 508–522.
- Cai, L.-M., Wang, Q.-S., Luo, J., Chen, L.-G., Zhu, R.-L., Wang, S., et al. (2019). Heavy metal contamination and health risk assessment for children near a large Cu-smelter in central China. *Science of the Total Environment*, 650, 725–733. <https://doi.org/10.1016/j.scitotenv.2018.09.081>.
- Cai, L. M., Xu, Z. C., Qi, J. Y., Feng, Z. Z., & Xiang, T. S. (2015). Assessment of exposure to heavy metals and health risks among residents near Tonglushan mine in Hubei, China. *Chemosphere*, 127, 127–135.
- Cao, S., Duan, X., Zhao, X., Ma, J., Dong, T., Huang, N., et al. (2014). Health risks from the exposure of children to As, Se, Pb and other heavy metals near the largest coking plant in China. *Science of the Total Environment*, 472(1), 1001–1009.
- CEME. (1990). *The Background Values of Chinese Soils*, China Environmental Monitoring Center. Beijing: China Environmental Science Press.
- Chen, H., Teng, Y., Lu, S., Wang, Y., & Wang, J. (2015). Contamination features and health risk of soil heavy metals in China. *Science of the Total Environment*, 512–513, 143–153.
- Chen, G., Wang, X., Wang, R., & Liu, G. (2019). Health risk assessment of potentially harmful elements in subsidence water bodies using a Monte Carlo approach: An example from the Huainan coal mining area, China. *Ecotoxicology and Environmental Safety*, 171, 737–745. <https://doi.org/10.1016/j.ecoenv.2018.12.101>.
- Chen, L., Zhou, S., Shi, Y., Wang, C., Li, B., Li, Y., et al. (2018). Heavy metals in food crops, soil, and water in the Lihe River Watershed of the Taihu Region and their potential health risks when ingested. *Science of the Total Environment*, 615, 141–149. <https://doi.org/10.1016/j.scitotenv.2017.09.230>.
- El Azhari, A., Rhoujjati, A., El Hachimi, M. L., & Ambrosi, J.-P. (2017). Pollution and ecological risk assessment of heavy metals in the soil-plant system and the sediment-water column around a former Pb/Zn-mining area in NE Morocco. *Ecotoxicology and Environmental Safety*, 144(5), 464–474.
- Entwistle, J. A., Hursthouse, A. S., Marinho Reis, P. A., & Stewart, A. G. (2019). Metalliferous Mine Dust: Human Health Impacts and the Potential Determinants of Disease

- in Mining Communities. *Current Pollution Reports*, 5(3), 67–83. <https://doi.org/10.1007/s40726-019-00108-5>.
- Fang, T., Lu, W., Cui, K., Li, J., Yang, K., Zhao, X., et al. (2019). Distribution, bioaccumulation and trophic transfer of trace metals in the food web of Chaohu Lake, Anhui, China. *Chemosphere*, 218, 1122–1130. <https://doi.org/10.1016/j.chemosphere.2018.10.107>.
- Fang, X., Tian, D. L., & Xie, R. X. (2006). Soil physical and chemical properties of the wasteland in Xiangtan manganese mine. *Acta Ecologica Sinica*, 26(5), 1494–1501.
- Hang, X., Wang, H., Zhou, J., Ma, C., Du, C., & Chen, X. (2009). Risk assessment of potentially toxic element pollution in soils and rice (*Oryza sativa*) in a typical area of the Yangtze River Delta. *Environmental Pollution*, 157(8), 2542–2549.
- Huang, M., Zhou, S., Sun, B., & Zhao, Q. (2008). Heavy metals in wheat grain: Assessment of potential health risk for inhabitants in Kunshan. *China. Science of the Total Environment*, 405(1), 54–61.
- Jiang, F., Ren, B., Hursthouse, A., Deng, R., & Wang, Z. (2019). Distribution, source identification, and ecological-health risks of potentially toxic elements (PTEs) in soil of thallium mine area (southwestern Guizhou, China). *Environmental Science and Pollution Research International*, 26(16), 16556–16567. <https://doi.org/10.1007/s11356-019-04997-3>.
- Jiang, F., Ren, B., Hursthouse, A. S., & Zhou, Y. (2018). Trace Metal Pollution in Topsoil Surrounding the Xiangtan Manganese Mine Area (South-Central China): Source Identification, Spatial Distribution and Assessment of Potential Ecological Risks. *Int J Environ Res Public Health*, 15(11), <https://doi.org/10.3390/ijerph15112412>.
- Li, Q., Chen, Y., Fu, H., Cui, Z., Shi, L., Wang, L., et al. (2012). Health risk of heavy metals in food crops grown on reclaimed tidal flat soil in the Pearl River Estuary. *China. Journal of Hazardous Materials*, 227–228(16), 148–154.
- Li, J. N., Li, J., hong, H., Wei, Y., Xu, Y. F., & Li, F. S. (2013). Bioaccessibility and Health Risk Assessment of Heavy Metals in Agricultural Soil from Zhuzhou, China. *Research of Environmental Sciences*, 26(10), 1139–1146.
- Li, Y., Yang, X., Bing, G., & Xue, L. (2018). Effective bioremediation of Cu(II) contaminated waters with immobilized sulfate-reducing bacteria-microalgae beads in a continuous treatment system and mechanism analysis. *Journal of Chemical Technology & Biotechnology*.
- Lian, M., Wang, J., Sun, L., Xu, Z., Tang, J., Yan, J., et al. (2019). Profiles and potential health risks of heavy metals in soil and crops from the watershed of Xi River in Northeast China. *Ecotoxicology and Environmental Safety*, 169, 442–448. <https://doi.org/10.1016/j.ecoenv.2018.11.046>.
- Liu, J., Cao, L., & Dou, S. (2017). Bioaccumulation of heavy metals and health risk assessment in three benthic bivalves along the coast of Laizhou Bay. *China. Marine Pollution Bulletin*, 117(1–2), 98–110.
- Liu, C. P., Luo, C. L., Gao, Y., Li, F. B., Lin, L. W., Wu, C. A., et al. (2010). Arsenic contamination and potential health risk implications at an abandoned tungsten mine, southern China. *Environmental Pollution*, 158(3), 820–826.
- Luo, X. S., Ding, J., Xu, B., Wang, Y.-J., Li, H.-B., & Yu, S. (2012). Incorporating bioaccessibility into human health risk assessments of heavy metals in urban park soils. *Science of the Total Environment*, 424(4), 88–96.
- Md Kawser, A., Nazma, S., Md Saiful, I., Md. H. A. M., Saiful, I., & Cadi Parvin, B. (2015). Trace elements in two staple cereals (rice and wheat) and associated health risk implications in Bangladesh. *Environmental Monitoring and Assessment*, 187(6), 326.
- Mehmood, A., Aslam Mirza, M., Aziz Choudhary, M., Kim, K. H., Raza, W., Raza, N., et al. (2019). Spatial distribution of heavy metals in crops in a wastewater irrigated zone and health risk assessment. *Environmental Research*, 168, 382–388. <https://doi.org/10.1016/j.envres.2018.09.020>.
- Ministry of Agriculture, P. (2004). *NY861-2004, Limits of Eight Elements in Crops*. Beijing: Ministry of Agriculture Press.
- Ministry of Health, P. (2006). *GB5749-2006, Standards for drinking water quality*. Beijing: Ministry Of Health, PRC.
- Ministry Of Health, P. (2012). *GB2762-2012, national food safety standards for food contaminants*. Beijing: Ministry Of Health, PRC.
- Pareja-Carrera, J., Mateo, R., & Rodríguez-Estival, J. (2014). Lead (Pb) in sheep exposed to mining pollution: Implications for animal and human health. *Ecotoxicology and Environmental Safety*, 108(108C), 210–216.
- Ren, B., Chen, Y., Zhu, G., Wang, Z., & Zheng, X. (2016). Spatial Variability and Distribution of the Metals in Surface Runoff in a Nonferrous Metal Mine. *Journal of Analytical Methods in Chemistry*, 2016(7), 1–11.
- Ren, B., Wang, Q., Chen, Y., Ding, W., & Zheng, X. (2015). Analysis of the Metals in Soil-Water Interface in a Manganese Mine. *Journal of Analytical Methods in Chemistry*, 2015(1), 163163.
- Sani, H. A., Ahmad, M. B., Hussein, M. Z., Ibrahim, N. A., Musa, A., & Saleh, T. A. (2017). Nanocomposite of ZnO with montmorillonite for removal of lead and copper ions from aqueous solutions. *Process Safety and Environmental Protection*, 109, 97–105.
- Shaheen, N., Irfan, N. M., Khan, I. N., Islam, S., Islam, M. S., & Ahmed, M. K. (2016). Presence of heavy metals in fruits and vegetables: Health risk implications in Bangladesh. *Chemosphere*, 152, 431–438.
- Sun, Z., Xiande, X., Ping, W., Yuanan, H., & Hefa, C. (2018). Heavy metal pollution caused by small-scale metal ore mining activities: A case study from a polymetallic mine in South China. *Science of the Total Environment*, 639, 217–227.
- USEPA. (1992). *Guidelines for Exposure Assessment*. Washington: Risk Assessment Forum.
- USEPA (2000). *Exposure Factors Handbook: Volume I-General Factors*. (Washington: Office of Research and Development National Center for Environmental Assessment).
- USEPA. (2005). *Guidelines for Carcinogen Risk Assessment*. Washington: Risk Assessment Forum.
- Vatanserver, R., Ozyigit, I. I., & Filiz, E. (2017). Essential and Beneficial Trace Elements in Plants, and Their Transport in Roots: a Review. *Applied Biochemistry and Biotechnology*, 181(1), 464–482.
- Wu, W., Wu, P., Yang, F., Sun, D. L., Zhang, D. X., & Zhou, Y. K. (2018). Assessment of heavy metal pollution and human health risks in urban soils around an electronics manufacturing facility. *Science of the Total Environment*, 630, 53.

- Xu, X., Cao, Z., Zhang, Z., Li, R., & Hu, B. (2016). Spatial distribution and pollution assessment of heavy metals in the surface sediments of the Bohai and Yellow Seas. *Marine Pollution Bulletin*, 110(1), 596–602.
- Yan, G., Mao, L., Liu, S., Mao, Y., Ye, H., Huang, T., et al. (2018). Enrichment and sources of trace metals in roadside soils in Shanghai, China: A case study of two urban/rural roads. *Science of the Total Environment*, s, 631–632, 942–950.
- Yujun, Y., Zhifeng, Y., & Shanghong, Z. (2011). Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. *Environmental Pollution*, 159(10), 2575–2585.
- Zhang Hui zhi, L. Y. g., HUANG Bao rong, LI Xin (2004). A survey of heavy-metal content in plants growing on the soil polluted by Manganese mine tailings. *cje*(1), 111-113.
- Zhang, J., Peng, B., & Gao, Z. (2011). The impact of urban land expansion on soil quality in rapidly urbanizing regions in China: Kunshan as a case study. *Environmental Geochemistry and Health*, 33(2), 125–135.
- Zhang, Y., Ren, B., Hursthouse, A. S., Deng, R., & Hou, B. (2018). An Improved SWAT for Predicting Manganese Pollution Load at the Soil-Water Interface in a Manganese Mine Area. *Polish Journal of Environmental Studies*, 27(5), 2357–2365. <https://doi.org/10.15244/pjoes/78618>.
- Zheng, N., Wang, Q., & Zheng, D. (2007). Health risk of Hg, Pb, Cd, Zn, and Cu to the inhabitants around Huludao Zinc Plant in China via consumption of vegetables. *Science of the Total Environment*, 383(1), 81–89.

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