



# Mercury pollution risks of agricultural soils and crops in mercury mining areas in Guizhou Province, China: effects of large mercury slag piles

Chengcheng Zhang · Tianxiang Xia · Lina Zhang ·  
Zhuo Chen · Haonan Zhang · Xiaoyang Jia ·  
Lin Jia · Xiaoying Zhu · Guangbing Li

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**Abstract** The historical large mercury slag piles still contain high concentrations of mercury and their impact on the surrounding environment has rarely been reported. In this study, three different agricultural areas [the area with untreated piles (PUT), the area with treated piles (PT), and the background area with no piles (NP)] were selected to investigate mercury slag piles pollution in the Tongren mercury mining area. The mercury concentrations of agricultural soils ranged from 0.42 to 155.00 mg/kg, determined by atomic fluorescence spectrometry of 146 soil samples; and mercury concentrations in local crops (rice, maize, pepper, eggplant, tomato and bean) all exceeded the Chinese food safety limits. Soil and crop pollution trends in the three areas were consistent as

PUT>PT>NP, indicating that mercury slag piles have exacerbated pollution. Mercury in the slag piles was adsorbed by multiple pathways of transport into soils with high organic matter, which made the ecological risk of agricultural soils appear extremely high. The total hazard quotients for residents from ingesting mercury in these crops were unacceptable in all areas, and children were more likely to be harmed than adults. Compared to the PT area, treatment of slag piles in the PUT area may decrease mercury concentrations in paddy fields and dry fields by 46.02% and 70.36%; further decreasing health risks for adults and children by 47.06% and 79.90%. This study provided a scientific basis for the necessity of treating large slag piles in mercury mining areas.

C. Zhang · T. Xia (✉) · L. Zhang (✉) · Z. Chen ·  
H. Zhang · X. Jia · L. Jia · X. Zhu  
National Engineering Research Center of Urban  
Environmental Pollution Control, Beijing Key Laboratory  
for Risk Modeling and Remediation of Contaminated  
Sites, Beijing Municipal Research Institute of Eco-  
Environmental Protection, Beijing 100037, China  
e-mail: xiatianxiang@cee.cn

L. Zhang  
e-mail: zhln2011@163.com

C. Zhang  
e-mail: 1811922676@qq.com

Z. Chen  
e-mail: 1143748217@qq.com

H. Zhang  
e-mail: 461996259@qq.com

X. Jia  
e-mail: jiaxiaoyang@cee.cn

L. Jia  
e-mail: jl\_0706@163.com

X. Zhu  
e-mail: zhuxiaoying@cee.cn

L. Zhang  
School of Environment, Beijing Normal University,  
Beijing 100875, China

G. Li  
Tongren Environmental Science and Technology  
Consulting Center, Tongren 554399, China  
e-mail: 260886247@qq.com

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## Introduction

Mercury (Hg) is a heavy metal in liquid form at ambient temperatures, and has high volatility, mobility, bioaccumulation, and toxicity (Pavithra et al., 2023). A total of  $1.54 \times 10^3$  kt of mercury were released by human activities by 2010; of this mercury, about  $1.07 \times 10^3$  kt were released to land and water bodies and  $3.5 \times 10^2$  kt were emitted directly into the atmosphere as  $\text{Hg}^0$  (Streets et al., 2017). Current anthropogenic emissions to air are  $2.5 \pm 0.5$  kt/y (Outridge et al., 2018). The mercury is mainly in the forms of mercury vapor, inorganic mercury, and organic mercury. Mercury vapor enters the human body through respiration and can cause serious damage to the central nervous system and immune system. Organic mercury ingested into the human body is easily absorbed by the gastrointestinal tract and then reaches various tissues and organs through blood circulation, mainly accumulating over time in the brain, liver, and kidneys (Clarkson, 1997; Kim et al., 2016; Kumar et al., 2022; Langford & Ferner, 1999). Mercury and its compounds can seriously harm the environment and human health. Several agencies such as the World Health Organization (WHO), the U.S. Environmental Protection Agency (USEPA), and the Ministry of Ecology and Environment of China (MEE) have listed it as a priority pollutant for control (MEE et al., 2017; Zheng et al., 2020).

Long-term mercury mining and smelting activities have caused severe environmental pollution in mercury mining areas. Early in the 21st century, mercury concentrations in sediments, surface water, and waste residues in abandoned mercury mining areas and the ecological effects of mercury raised concern (Gray et al., 2000, 2002, 2003). With increasing emphasis on environmental protection, the concentrations, morphology, distribution, and transport of mercury in mercury mining areas and the surrounding environment have been extensively studied in China (Li et al., 2008; Lin et al., 2010; Qiu et al., 2005, 2006a, 2006b; Xia et al., 2016; Yan et al., 2019; Zhang et al., 2009). Meanwhile, research on the health of residents in mercury mining areas has begun. Feng et al. (2008) assessed the dietary exposures of residents

to methylmercury and verified that rice is a major source of exposure. Jia et al. (2018) verified that vegetables are also a major source of exposure by exploring the relationship between methylmercury concentrations in residents' hair and consumption of vegetables. The Minamata Convention on Mercury, which aims to reduce the damage caused by mercury to the environment and human health, entered into force on 16 August 2017, and the quantitative identification and management of risks at mercury-polluted sites received initial attention (Coulter, 2016). Some studies have begun to use the multimedia multi-pathway exposure assessment (MMPA) models in association with probabilistic risk analysis software for human health risk studies in abandoned mercury mining areas. Jimenez-Oyola et al. (2020) found that the health risk contributions of vegetable ingestion, mushroom ingestion and fish ingestion were 79.0%, 0.78% and 15.1%, respectively, at the historical largest mercury mining area in Spain. Xu et al. (2020) also found that the health risk contributions of inorganic mercury (IHg) intake through consumption of rice, vegetables, maize and agricultural products (pork, poultry and fish) in the Wanshan mercury mining area were 5.1%, 59.1%, 0.20% and 37.8%, respectively; and those of methylmercury (MHg) intake were 87.5%, 1.4%, 0.79% and 10.4%, respectively. Therefore, agricultural products from mercury mining areas are an important source of mercury intake for the residents.

China's mercury resources are mainly concentrated in Guizhou Province, where the Tongren mercury mine is one of the largest mercury producing areas in China. Operation of this mine ceased in 2001 due to exhausted mercury resources and environmental problems (Du et al., 2021; Li et al., 2013; Qiu et al., 2005; Yan et al., 2019). In 2016, China's Ministry of Ecology and Environment conducted a survey and found that the amount of about  $5.2 \times 10^3$  kt of waste residues were produced at the Tongren mercury mine, containing approximately  $5.3 \times 10^2$  kt of mercury, the average mercury concentration in the waste residues was 101.92 mg/kg (MEE, 2016). The mercury concentrations of waste residues ranged from 43 to 660 mg/kg in the Palawan Quicksilver Mine, Philippines (Gray et al., 2003), and mercury concentrations of waste residues ranged from 4.15 to 825 mg/kg in the Wanshan and Tongren mining areas, China (Yan et al., 2019). With the cessation of smelting and other

activities at the mercury mining areas, the remaining mercury open slag piles without treatment measures have become a local source of pollution that cannot be ignored (Warchulski et al., 2015). The residual mercury in these slag piles can be transported into the environment through rainfall and weathering, causing serious pollution to the surrounding soil, sediment, water, and crops and further endangering the health of local residents (Opiso et al., 2018); while the environmental problems caused by large mercury slag piles have received little attention.

In this study, we selected three agricultural areas (PUT, PT, and NP areas) affected by different sources of pollution to carry out a survey of soils, crops, and irrigation water. The PUT, PT, and NP areas were all affected by historical long-term mercury mining activities. There is currently a large untreated mercury slag pile surrounding the PUT area and there are two treated mercury slag piles surrounding the PT area. The main objectives of this study were to: (1) investigate mercury pollution of agricultural soils and crops; (2) main factors influencing the transport of mercury into soil; (3) assess ecological and health risks; and (4) quantify the environmental and health benefits of treating mercury slag piles.

## Materials and methods

### Study area

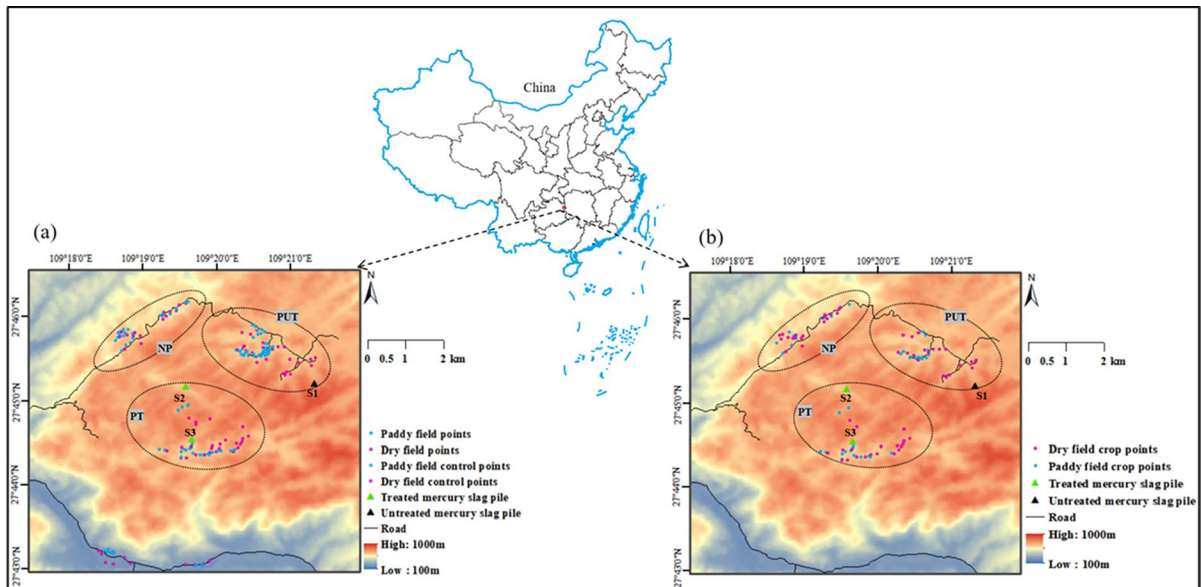
The study area is located in the eastern part of Tongren city, at the junction of Hunan and Guizhou Provinces. The area has a subtropical monsoon warm and humid climate, with both plateau and monsoon climate characteristics, with four distinct seasons and simultaneous rain and high-temperature. The average annual temperature is 15 °C, the annual frost-free period is about 250 d, the average annual rainfall is 1250 mm, and the annual sunshine hours are 1050 h. This area is located on the transitional slope from the Guizhou plateau to the hills of the western Hunan region, so low hills are widespread, with higher elevation in the southeast and lower in the northwest. The main types of farmland are paddy fields and dry fields; the average altitude of the paddy fields is 595 m, while the average altitude of the dry fields is 607 m. Rice is the main crop grown in paddy fields; maize and vegetables such as pepper and tomato

are the main crops grown in dry fields. Local irrigation water for agriculture comes mainly from small streams.

A 2022 on-site investigation and historical data collection found that there are three mercury slag piles in the study area, each containing waste residues exceeding  $1.0 \times 10^3$  kt. An untreated slag pile was identified as Slag Pile 1, with about  $3.55 \times 10^3$  kt of waste residues that has been stockpiled in the open for approximately 20 years. The other two slag piles were identified as Slag Pile 2 and Slag Pile 3, at which preliminary treatment was completed around 2018; Slag Pile 2 and Slag Pile 3 contain approximately  $4.35 \times 10^3$  and  $1.26 \times 10^3$  kt of waste residues, respectively. The engineering treatment technology adopted was in-situ restoration, including centralized consolidation of mercury slag piles, construction of slag retaining walls, and flood interception ditches. An anti-seepage layer and drainage layer were laid down, with a surface layer protected by a grid framework and covered with soil for ecological restoration.

### Sampling and analysis

This study set the initial survey distance to 1.5 km based on three main factors: the storage time of slag piles, the average annual rainfall, and the average annual wind speed, and expanded the survey area around Slag Pile 1 to 2.5 km, considering that it was untreated. The sampling points in the PUT area were within 2.5 km of Slag Pile 1, those in the PT area were within 1.5 km of Slag Pile 2 or Slag Pile 3, and those in the NP area were 1.5 km away from the nearest Slag Pile 2. Considering the scattered distribution of farmland in the study area, a combination of grid and random sampling methods was used to ensure that soil sampling points were placed in each agricultural area (Fig. 1a); approximately 1 kg of surface soil (0–20 cm) was collected at each sampling point. Soil samples were collected from both paddy fields and dry fields, and some soil samples were collected outside the mercury mine area as control samples, more than 3 km from the nearest mercury slag pile. Agricultural irrigation water samples were also collected in the paddy field areas. In addition, 15 rice samples, 9 maize samples, and 3 samples of each vegetable were collected from each area (Fig. 1b); Only edible parts were taken from each crop. The types of vegetables collected were pepper, eggplant, tomato, and



**Fig. 1** Distribution of agricultural soil and crop sampling points. **a** Agricultural soil sampling points; **b** crop sampling points. S1, S2, and S3 represent Slag Pile 1, Slag Pile 2, and Slag Pile 3, respectively. The polluted area (PUT) represents the agricultural area surrounding the untreated mercury slag pile; the treated area (PT) represents the agricultural area sur-

rounding mercury slag piles for which treatment has been completed; and the background area (NP) represents an agricultural area without mercury slag piles. The black dashed circles show the sampling areas for agricultural soil and crops relative to the mercury slag piles

bean. Approximately 0.5 kg of each crop sample was collected and taken to the laboratory along with the soil and water samples for further processing.

Soil samples were taken to the laboratory and naturally dried in a cool place. After removing stones, plant and animal debris with tweezers, the soil was ground with a mortar, passed through a 0.149 mm nylon mesh screen, and stored in a self-sealing polyethylene bag. The collected crop samples were washed with tap water and then deionized water, dried in an oven at 55 °C, ground, and stored in a self-sealing polyethylene bag. Determination of soil pH using a HI 2210 benchtop pH meter with a water-soil ratio of 2.5:1, organic matter was determined based on the potassium dichromate volumetric method, and cation exchange capacity was determined using the EDTA-ammonium acetate exchange method (Woldeyohannis et al., 2022). Soil and crop samples were heated in a boiling water bath using a nitric acid-hydrochloric acid reagent mixture, and then the mercury in solution was reduced to atomic mercury using potassium

borohydride, which was carried by a carrier gas into an atomic fluorescence spectrometer equipped with a mercury hollow cathode lamp for determination. ((MEE, 2008; MoH, 2021). Agricultural irrigation water was unfiltered and the samples were digested in sulphuric acid with a potassium bromate-potassium bromide mixture under heating conditions, then the excess oxidant was reduced with hydroxylamine hydrochloride, and the divalent mercury was reduced to metallic mercury with stannous chloride; the metallic mercury was vapourized with nitrogen at room temperature and loaded into a cold atomic absorption mercury analyser for determination at 253.7 nm (MEE, 2011).

To ensure reliable analytical results, one duplicate sample was measured for every 10 samples and the relative standard deviations were found to be less than 10%. Blank samples and standard materials were also analyzed for mercury (standard sample number GBW 07404 (GSS-4)) with recoveries ranging from 95 to 105%.

Evaluation and assessment methods

*Geoaccumulation index*

The geoaccumulation index ( $I_{geo}$ ) is based on soil background or other reference values used to evaluate the level of pollution in the organic or humic layer of the soil (Kowalska et al., 2018; Muller, 1969), generally considered to be the topsoil (0–20 cm deep). The formula is:

$$I_{geo} = \log_2 \left[ \frac{C_i}{K \times C} \right] \tag{1}$$

where  $C_i$  is the measured mercury concentration of the soil (mg/kg),  $C$  is the background value (0.11 mg/kg) of mercury in soil of Guizhou Province (Lin et al., 2012), and  $K$  is a correction factor representing the influence of soil characteristics, geology, and other factors (a value of 1.5 was selected for this study). The  $I_{geo}$  result is assessed on a relative scale to evaluate the level of soil pollution (Table 1).

*Potential ecological risk index*

The potential ecological risk index ( $E_i$ ) was proposed by Hakanson in 1980 to assess the ecological risks of heavy metal concentrations in water, air, or soil (Hakanson, 1980).  $E_i$  integrates heavy metal toxicity and environmental effects and is one of the most widely used methods to assess the degree of heavy metal pollution. The calculation formula is:

$$E_i = T_i \times \frac{C_i}{C} \tag{2}$$

where  $T_i$  is the toxicity coefficient for the heavy metal (40 for mercury),  $C_i$  is the mercury concentration in the surface soil (mg/kg), and  $C$  is the background value (0.11 mg/kg) of mercury in soil of

Guizhou Province. The calculated results are combined with the potential ecological risk classification to evaluate the risk level (Table 1).

*Health risk assessment*

Numerous studies have shown that the primary pathway of mercury exposure for residents of mercury mining areas is through dietary intake (Jimenez-Oyola et al., 2020; Marrugo-Madrid et al., 2022; Xu et al., 2020). Combined with the local dietary habits in the study area, crops consumed by the residents on a daily basis were selected for assessment, and the average daily intake of mercury was calculated based on the USEPA (2019) exposure assessment model. The calculation formula is:

$$Q = \frac{C \times IR}{BW} \times 10^{-3} \tag{3}$$

where  $Q$  is the average daily intake of mercury by local residents through consumption of a specific crop ( $\mu\text{g}/\text{kg}\cdot\text{d}$ );  $C$  is the mercury concentration in the crop ( $\mu\text{g}/\text{kg}$ ),  $IR$  is the average daily ingestion of a specific crop (g/d), and  $BW$  is the average body weight of adults or children (kg). The values for all parameters are shown in Table 2.

Mercury has only noncarcinogenic effects and its hazard quotient is calculated using the formula:

$$HQ = \frac{Q}{RfD} \tag{4}$$

$$HI = \sum HQ \tag{5}$$

where  $HQ$  is the hazard quotient for mercury intake through the consumption of a specific crop,  $RfD$  is the average daily allowable intake of mercury ( $\mu\text{g}/\text{kg}\cdot\text{d}$ ), the value for  $RfD$  is shown in Table 2; and  $HI$  is the total hazard quotient. When the HI is greater

**Table 1** Geoaccumulation index and potential ecological risk index classifications

Geoaccumulation index	Degree of pollution	Index of potential ecological risk	Risk level
$I_{geo} \leq 0$	Clean	$E_i < 40$	Low
$0 < I_{geo} \leq 2$	Low to moderate	$40 \leq E_i < 80$	Moderate
$2 < I_{geo} \leq 4$	Moderate to high	$80 \leq E_i < 160$	High
$4 < I_{geo} \leq 5$	High to extremely high	$160 \leq E_i < 320$	Very high
$5 < I_{geo} \leq 10$	Extremely high	$E_i \geq 320$	Extremely high



**Table 2** Exposure parameter values for adults and children

Parameter	Unit	Meaning	Adult	Children	References
$IR_{rice}$	g/d	Daily ingestion of rice	Normal (mean = 313.7, SD = 25.49)	Normal (mean = 163.2, P95 = 326.7)	Duan et al., (2014); Duan et al., (2016)
$IR_{maize}$	g/d	Daily ingestion of maize	Mean = 70	Mean = 50	Xu et al., (2020)
$IR_{vegetables}$	g/d	Daily ingestion of vegetables	Normal (mean = 342.3, SD = 22.19)	Normal (mean = 167.4, P95 = 329.9)	Duan et al., (2014); Duan et al., (2016)
$BW$	kg	Body weight	Normal (mean = 55.9, P95 = 73.5)	Normal (mean = 19.3, P95 = 24.9)	Duan et al., (2014); Duan et al., (2016)
$RfD$	$\mu\text{g}/\text{kg}\cdot\text{d}$	Daily allowable intake of mercury	Mean = 0.47	Mean = 0.23	FAO/WHO (2007)

P95 is the 95th percentile

than 1, the health risk is unacceptable and may be harmful to humans; conversely, at or below 1, the health risk is acceptable.

A probabilistic estimate was obtained using Oracle Crystal Ball software by Monte Carlo simulation to reduce the uncertainty in the risk assessment (Jafarzadeh et al., 2022; Jimenez-Oyola et al., 2020; Xu et al., 2020). The Monte Carlo simulation was run at the 95% confidence level. Values for each variable were randomly selected based on their distribution functions. Probabilistic sensitivity analysis utilizing Monte Carlo simulations was conducted with 10,000 iterations.

## Results and discussion

### Mercury pollution in agricultural area

#### Mercury concentrations in agricultural soil

Mercury concentrations in agricultural soil ranged from 1.54 to 155.00 mg/kg (Table 3), the average mercury concentration was  $29.88 \pm 32.94$  mg/kg; while soil mercury concentrations ranged from 3.06 to  $2.92 \times 10^3$  mg/kg in the Tongren mercury mining area, the average mercury concentration was 322 mg/kg (Xia et al., 2016). Soil mercury concentration was

**Table 3** Distributions of mercury concentrations and physicochemical properties of agricultural soils

Soil index	Type of farmland	Samples	Min	Med	Max	Mean	SD	CV (%)
Mercury concentrations	Paddy fields	Study area ( $N=74$ )	1.54	24.39	155.00	37.63	37.96	100.89
		PUT area ( $N=33$ )	6.41	35.20	155.00	55.06	45.72	83.03
		PT area ( $N=23$ )	5.64	16.00	99.40	29.72	25.14	84.58
		NP area ( $N=18$ )	1.54	9.33	47.90	15.78	13.06	82.80
		CS ( $N=10$ )	0.12	0.23	0.31	0.23	0.05	22.81
	Dry fields	Study area ( $N=63$ )	1.94	11.20	92.60	20.78	22.67	109.08
		PUT area ( $N=25$ )	7.30	24.40	92.60	37.49	28.53	76.09
		PT area ( $N=23$ )	1.94	9.53	31.60	11.11	7.71	69.42
		NP area ( $N=15$ )	2.50	7.34	19.80	8.41	5.20	61.84
		CS ( $N=10$ )	0.07	0.12	0.21	0.13	0.04	34.87
Physicochemical properties	Paddy fields	pH ( $N=11$ )	6.34	7.76	8.35	7.59	0.65	8.56
		OM ( $N=11$ )	44.30	63.20	109.00	70.77	18.81	26.58
		CEC ( $N=11$ )	13.40	14.65	17.80	15.06	1.53	10.15
	Dry fields	pH ( $N=14$ )	5.66	7.62	8.65	7.35	0.87	11.79
		CEC ( $N=14$ )	5.82	11.85	17.40	11.68	3.16	27.03

Units: mercury concentrations, mg/kg; organic matter, g/kg; CEC, cmol/kg.  $N$  is the number of soil samples. CS is the control sample

significantly decreased by 90.72%, mainly due to the treatment of tailings and large slag piles, continuous accumulation of mercury in the soil by crops (Hang et al., 2016), and transport of mercury from the soil to other environmental media (O'Connor et al., 2019). Xia et al. (2021) estimated mercury efflux from a Karst region in Southwest China and found that the pathways for mercury export from the Huilong catchment were underground runoff ( $10.6 \pm 0.45 \text{ ug/m}^2 \cdot \text{y}$ ), surface runoff ( $11.0 \pm 0.48 \text{ ug/m}^2 \cdot \text{y}$ ), crops harvesting ( $462 \pm 66.4 \text{ ug/m}^2 \cdot \text{y}$ ), and air–soil surface  $\text{Hg}^0$  exchange ( $1.23 \times 10^3 \pm 1.31 \times 10^3 \text{ ug/m}^2 \cdot \text{y}$ ).

The average pH of paddy field soils was  $7.59 \pm 0.65$  and that of dry field soils was  $7.35 \pm 0.87$ ; demonstrating that the soil in this area is neutral to alkaline. The average organic matter (OM) content of paddy field and dry field soils were  $70.77 \pm 18.81 \text{ mg/kg}$  and  $25.91 \pm 8.11 \text{ mg/kg}$ , respectively; their average cation exchange capacities (CEC) were  $15.06 \pm 1.53 \text{ cmol/kg}$  and  $11.68 \pm 3.16 \text{ cmol/kg}$ , respectively. The average soil mercury concentrations in paddy fields and dry fields were  $37.63 \pm 37.96 \text{ mg/kg}$  and  $20.78 \pm 22.67 \text{ mg/kg}$ , respectively. Mercury concentrations in paddy fields in the study area were significantly higher than those ( $8.80 \pm 5.68 \text{ mg/kg}$ ) reported by Du et al (2021) in the Wanshan mercury mining area. Liu et al. (2021) also found the highest mercury concentrations ( $2.92 \times 10^3 \text{ mg/kg}$ ) in the soil around the Tongren mercury mining area. Mercury concentrations in agricultural soils were significantly higher than those at the control points, indicating that previous mercury mining activities and long-term open slag piles had caused serious pollution of the surrounding agricultural land. In addition, the soil mercury concentrations in paddy fields were significantly higher than those in dry fields, consistent with the results of Yin et al. (2016), suggesting that higher soil mercury concentrations in paddy fields than in dry fields may be common in southwest China. Compared with the background values of soil mercury in Guizhou Province ( $0.11 \text{ mg/kg}$ ) and China ( $0.02\text{--}0.2 \text{ mg/kg}$ ) (Lin et al., 2012), the dry fields mercury concentration in the control site was similar, while the paddy fields mercury concentrations in the control sites was higher than the background values.

Comparing the mercury concentrations in agricultural soil in the three areas, the average mercury concentrations in the paddy fields were  $\text{PUT} > \text{PT} > \text{NP}$ , with similar trends observed for dry fields. These

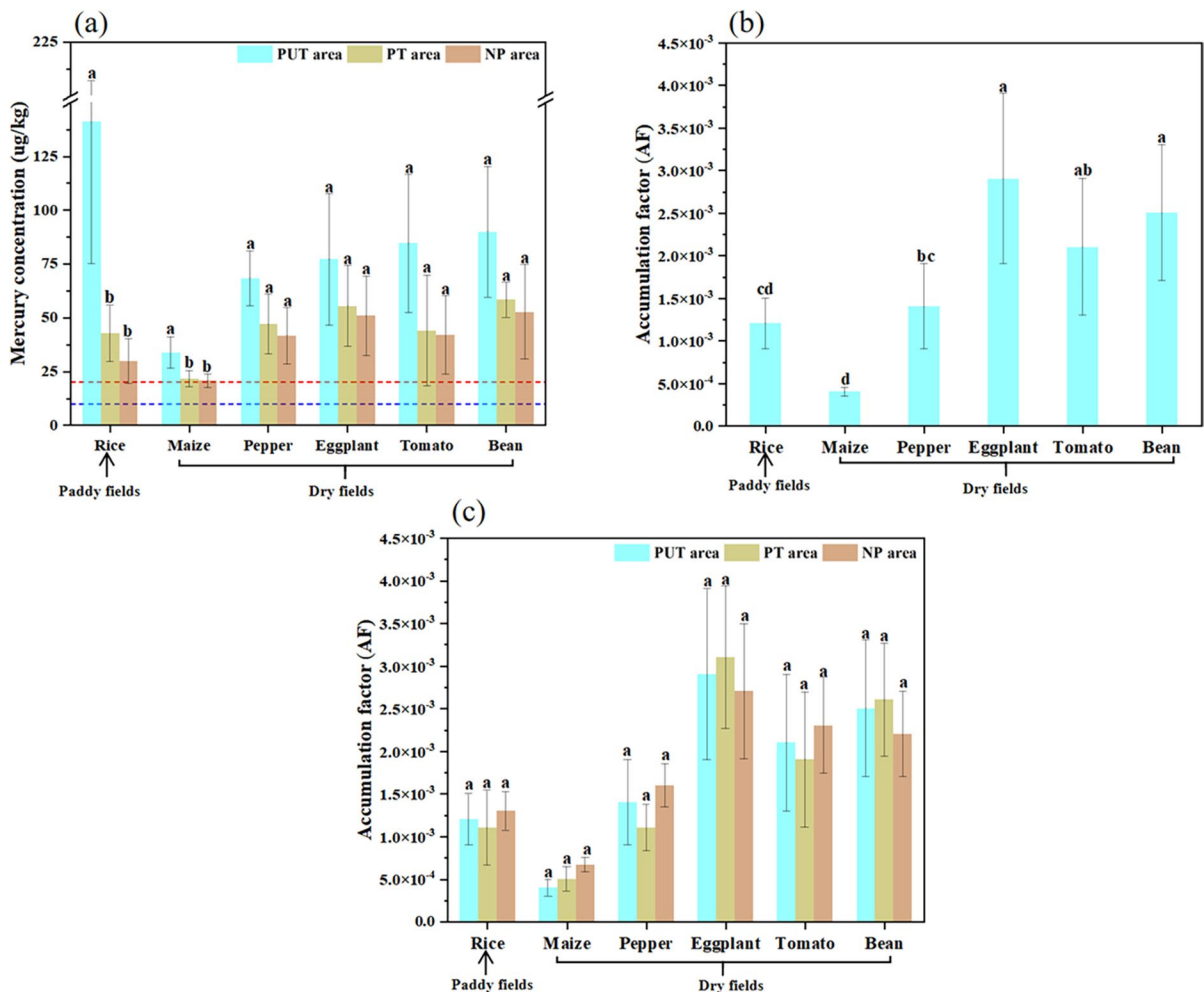
results indicate that mercury pollution in agricultural land is most serious in the PUT area, followed by the PT area and the NP area. Because the agricultural land in the NP area is relatively far from the three slag piles, while there were slag piles surrounding the agricultural land in the PUT and PT areas, the latter were more severely polluted than the NP area, indicating significant pollution of surrounding agricultural soils by mercury slag piles. Slag Pile 1 had not yet been treated, while Slag Piles 2 and 3 had previously completed preliminary treatment. In addition, due to the high elevation of Slag Pile 1, the mercury in that slag pile was more easily transported downstream into the farmland of the PUT area, resulting in soil mercury concentrations in paddy fields and dry fields that were 3.49 and 4.46 times higher than those in the NP area, respectively. Although there were no mercury slag piles surrounding the NP area, the mercury concentrations in soils were much higher than at the control points, which may be attributed to historical long-term mercury mining activities. Based on the current mercury concentrations in agricultural soils in the PT area, once treatment of Slag Pile 1 is completed, the mercury concentrations in the paddy fields and dry fields in the PUT area could be decreased by 46.02% and 70.36%, respectively. Yan et al. (2019) found that concentrations of mercury in surface water and atmospheric in the vicinity of the treated mercury slag piles in the Wanshan mercury mining area were obviously lower than those in the Tongren mercury mining area. These results suggest that the benefits of mercury slag pile management are significant in terms of reducing pollution of the surrounding environment.

#### *Mercury concentrations and accumulation in crops*

Heavy metals such as mercury that enter agricultural soils are transported into crops and vegetables, which take up some of the mercury in the soil through their root systems, causing mercury to accumulate in the roots, stems, leaves, and fruits of the plants (Li et al., 2017; Xia et al., 2020; Yang et al., 2020). The present study found that the average mercury concentrations in rice, maize, peppers, eggplants, tomatoes, and beans collected from all three areas exceeded the Chinese food safety limits (MoH, 2022) (Fig. 2a). The mercury concentrations in maize samples from Wukeng and Zhangjiawan in the Wanshan

mercury mining area were  $21.55 \pm 32.67 \mu\text{g}/\text{kg}$  and  $21.61 \pm 7.49 \mu\text{g}/\text{kg}$  (Sun et al., 2019), respectively, similar to the mercury concentrations in maize from the PT and NP areas. However, mercury concentrations in maize from the PUT area were higher than the results of previous studies. Mercury concentrations in the remaining crops were similar to the results of a screening study of crops with low mercury accumulation conducted by Xia et al (2020) in the Wanshan mercury mining area.

The mercury concentrations in rice and maize from the PUT area were both significantly higher than those in the other areas, while the mercury concentrations in the other crops did not differ significantly among the three areas. In general, the PUT area had the highest mercury concentrations in crops, followed by the PT and NP areas, consistent with the pattern of mercury pollution in agricultural soil. The accumulation factor (AF) is defined as the ratio of the mercury concentration in the crops to that in the agricultural soils (Wang et al., 2021). The AFs for



**Fig. 2** Comparison of crops mercury concentrations based on dry weight and accumulation factors. **a** Crops mercury concentrations based on dry weight; the red dashed line indicates the safety limit (20 ug/kg) for food crops; the blue dashed line indicates the food safety limit (10 ug/kg) for vegetable crops. The letters a and b indicate the presence or absence of

significant differences based on one-way analysis of variance (ANOVA,  $p < 0.05$ ), with the same letter indicating no significant difference and different letters indicating a significant difference, **b** comparison of accumulation factors for different crops, **c** comparison of accumulation factors for the same crop in different areas



rice, maize, pepper, eggplant, tomato and bean were  $1.2 \times 10^{-3}$ ,  $4.0 \times 10^{-4}$ ,  $1.4 \times 10^{-3}$ ,  $2.9 \times 10^{-3}$ ,  $2.1 \times 10^{-3}$  and  $2.5 \times 10^{-3}$ , respectively; and the highest AF was found for eggplant and the lowest for maize, and the accumulation factors of eggplant and bean were significantly higher than those of rice, maize, and pepper (Fig. 2b). Comparison of the AF for each crop revealed no differences among the three areas (Fig. 2c), suggesting that the magnitude of the AF for these crops may not be influenced by the degree of pollution in the planting soils, but rather by the crop species. Xia et al. (2020) found that most crops have mercury accumulation factors in the range of  $1 \times 10^{-2}$  to  $1 \times 10^{-4}$ . Although most crops have low mercury accumulation capacity, if they were planted in agricultural land with high mercury pollution, their edible parts can nevertheless have high mercury concentrations. It has been reported that the mercury concentration in paddy fields was positively correlated with the mercury concentration in rice grains, confirming that paddy field soil was the main source of mercury to the crops (Li, 2013; Tang et al., 2020). Therefore, screening of crops with low mercury accumulation capacity should be conducted and treatment of mercury pollution in farmland is necessary.

Main factors affecting the transport of mercury to soil

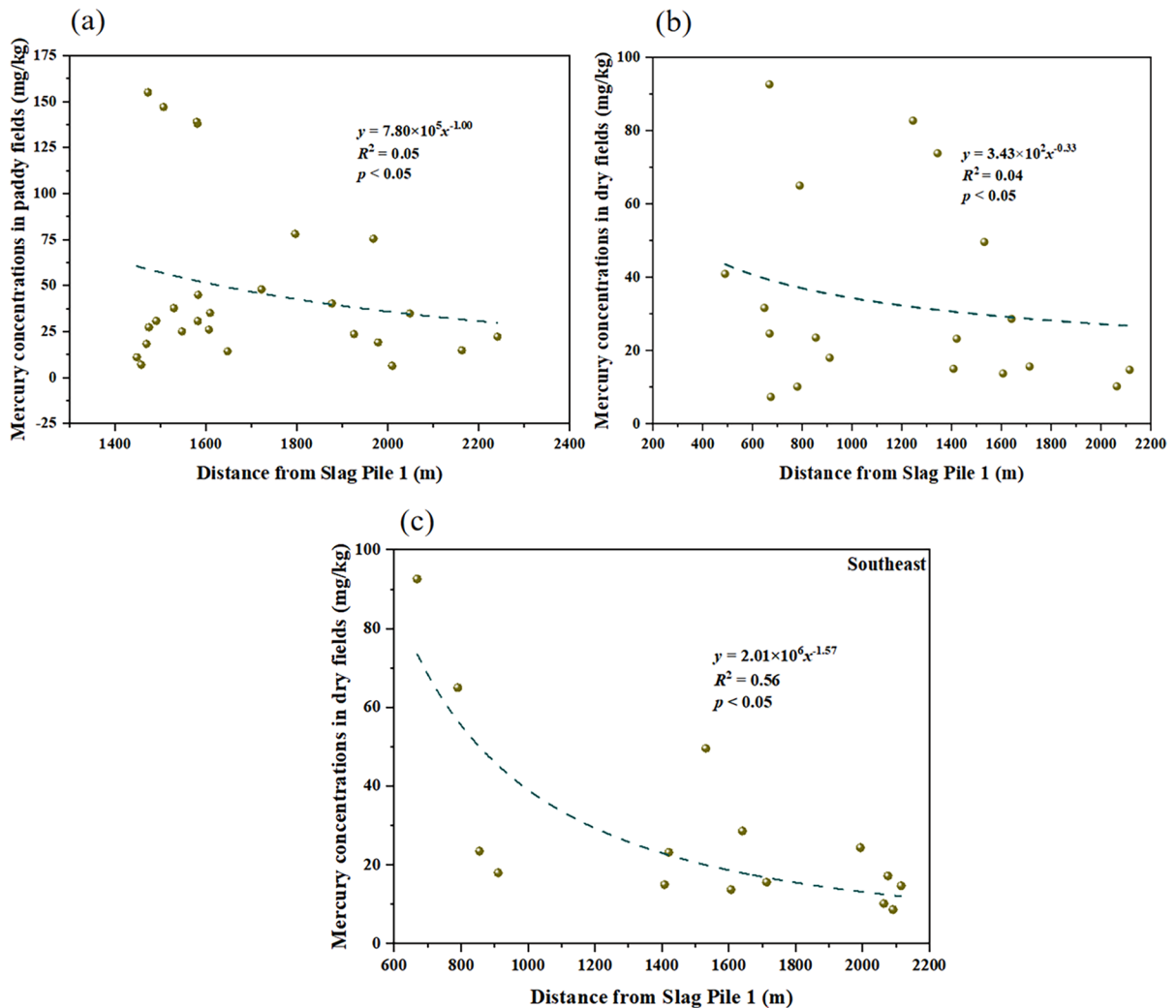
#### *Transport pathways of mercury*

Mercury from pollution sources may reach agricultural land through atmospheric deposition (Feng & Qiu, 2008; Hou et al., 2016; Liang et al., 2017; Liu et al., 2021; Zhang et al., 2018), agricultural irrigation (Wang et al., 2016; Xu et al., 2023) and rainfall runoff (Liu et al., 2021). Many studies confirmed that mine wastes were important mercury emission sources to the atmosphere. Li et al. (2013) found the average proportion of  $\text{Hg}^0$  in mine wastes from Chinese mercury mines to be 34.5% and showed this form of mercury would be expected to slowly evaporate into the atmosphere. The mercury emission fluxes from waste residues reached  $5.72 \text{ ug/m}^2\cdot\text{h}$  in the Wanshan mining area and the annual emission achieved 1.0–5.0 kg (Wang et al., 2007). Yan et al. (2019) found about 46.0% of  $\text{Hg}^0$  in the mercury mine waste residues from Tongren and the concentration of total gaseous mercury (TGM) ranged from 13.5 to 309  $\text{ng/m}^3$ , which is elevated compared with the background

global value (1.5–1.6  $\text{ng/m}^3$ ) and TGM at Guiyang city (8  $\text{ng/m}^3$ ).

The multiplicative power function ( $y=a*x^b$ ) has been used to study the transport patterns of mercury pollution with satisfactory results (Feng et al., 2006; Morosini et al., 2021). Using non-linear fitting (Fig. 3a), variations in soil mercury concentrations with distance to the paddy fields near Slag Pile 1 were relatively small ( $R^2=0.05$ ), but the overall trend showed a slight decrease with increasing distance from Slag Pile 1. One factor affecting these results may be that there are no paddy fields within 1.4 km of Slag Pile 1, resulting in a lack of data. There are also several potential transport pathways for mercury to enter the paddy fields, making it difficult to identify a pattern of variation with distance. Fitting the dry field soil mercury concentration trend with distance around Slag Pile 1 (Fig. 3b) indicated that the results for dry fields were nearly the same as those for paddy fields ( $R^2=0.04$ ). Considering that the primary transport pathway from the slag pile to the dry fields may be atmospheric deposition and taking into account the wind direction, the results of the fitting (Fig. 3c) identified a more obvious trend in the soil mercury concentration with distance ( $R^2=0.56$ ). The present study found that mercury concentrations in dry fields varied significantly with distance in the south-east wind direction. Considering atmospheric deposition as one of the pathways for agricultural soils, and combined with the results of Li et al. (2013) and Yan et al. (2019), it was hypothesized that large slag piles have significantly polluted surrounding agricultural land through atmospheric deposition.

Comparing the mercury concentrations in the irrigation water of paddy fields in the three areas (Table 4), the mercury concentration in the irrigation water of paddy fields in the PUT area was the highest ( $1.41 \pm 1.43 \text{ ug/L}$ ), which was lower than mercury concentration of Waters-unfiltered ( $6.0 \pm 1.5 \text{ ug/L}$ ) from abandoned mercury mines in West-Central Nevada, USA (Gray et al., 2002), while exceeded the standard for irrigation water quality (1.0  $\text{ug/L}$ ) (MEE, 2021); the agricultural irrigation water comes from surface water such as small streams, the concentration of mercury in the surface water that flowed through the mine wastes ranged from 0.038 to 10.6  $\mu\text{g/L}$  in the Tongren mercury mining area (Yan et al., 2019), and mercury in surface waters ranged from 0.019 to 12  $\mu\text{g/L}$  in the Wanshan mercury mining area (Qiu



**Fig. 3** Correlation and variation in soil mercury concentrations with distance. **a** Paddy field soil points in all directions, **b** dry field soil points in all directions, **c** dry field soil points in the southeast direction

**Table 4** Distributions of mercury concentrations in agricultural irrigation water ( $\mu\text{g/L}$ )

Area	Minimum	Maximum	Mean	SD	SV (%)	Limit value
PUT area ( $N=10$ )	0.48	5.35	1.41	1.43	101.45	1.00
PT area ( $N=10$ )	0.18	0.66	0.33	0.15	46.01	1.00
NP area ( $N=10$ )	0.06	0.25	0.14	0.06	45.67	1.00

The limit value is the standard for irrigation water quality,  $N$  is the number of water samples

et al., 2009), which have been shown to be polluted with mercury in surface water at the mining area. Using isotope tracing, Yan et al. (2023) found that mine waste was a significant source of mercury

pollution in local aquatic ecosystems, accounting for  $49.3 \pm 11.9\%$  and  $37.8 \pm 11.8\%$  of river dissolved mercury in high flow period and low flow period, respectively. Liu et al. (2022) found that the altitude

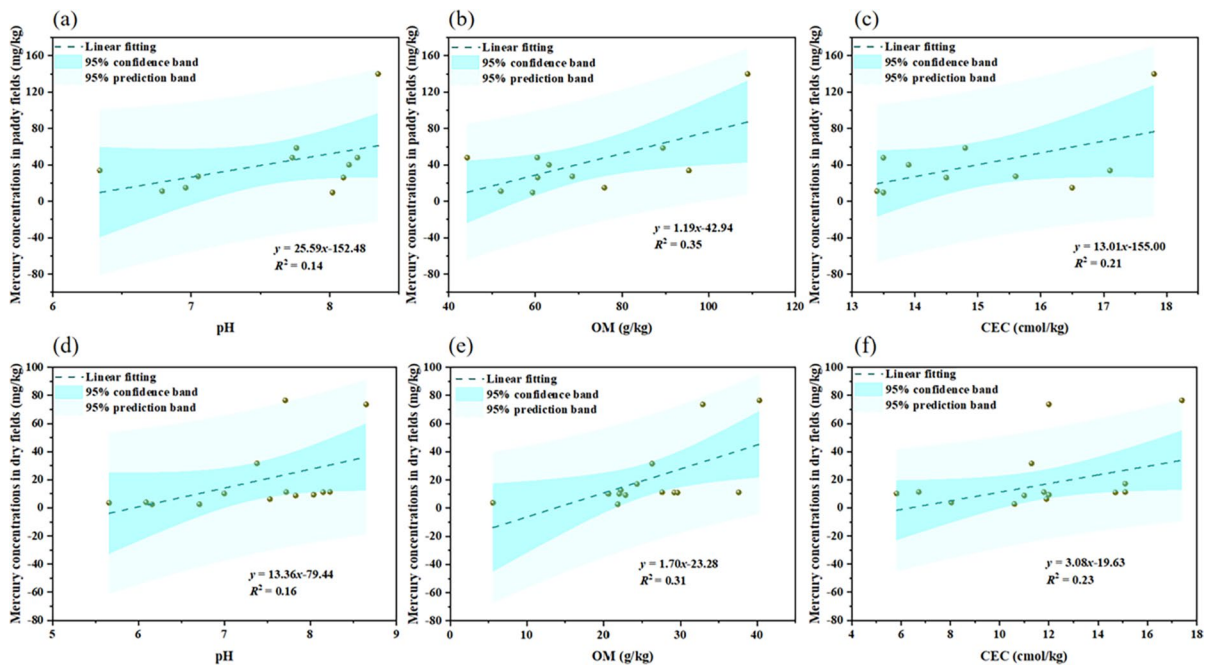
of paddy fields was generally lower than that of dry fields in the Wanshan mercury mining area, and that agricultural irrigation and heavy rainfall runoff (mainly torrential flood) were the main pathways for mercury transport to paddy fields, with the contribution of hydraulic transport ranging from 69.8% to 83.8%; and that the contribution of atmospheric deposition was relatively small (11.1%–16.1%). Therefore, differences in mercury transport pathways from the slag piles may be one of the factors leading to higher mercury concentrations in paddy fields than in dry fields.

*Physicochemical properties of the soil*

Heavy metals transported to agricultural land are involved in adsorption–desorption processes in soil (Jing et al., 2018; Yu et al., 2023). A linear fitting of pH, organic matter, and CEC vs. soil mercury concentrations for each of the two types of agricultural soils showed that pH was weakly correlated with mercury concentrations in paddy fields ( $R^2=0.14$ ,  $p<0.05$ ) and dry fields ( $R^2=0.16$ ,  $p<0.05$ ) (Fig. 4a, d). Studies have shown that there is a correlation between soil mercury concentration and pH, which

is attributed to the influence of soil pH on adsorption–desorption of mercury (Jiang et al., 2012). An increase in pH generally increases the negative charge on the surface of clay minerals and organic matter, resulting in a change from electrostatic adsorption to more site-specific adsorption with stronger binding. This change increases the stability of organic matter–Hg complexes and reduces the desorption of mercury, increasing mercury concentrations in farmland soil over time (Carvalho et al., 2019).

OM in paddy fields and in dry fields was also correlated with the mercury concentration in agricultural soil ( $R^2=0.35$ ,  $p<0.05$  and  $R^2=0.31$ ,  $p<0.05$ , respectively) (Fig. 4b, e). The positive correlation between soil organic matter and mercury concentrations in agricultural soil has also been observed in previous studies (Chen et al., 2012; Hang et al., 2016). Linde et al. (2007) used a multiscale geochemical model and found that soil organic matter is an important adsorbent for heavy metals such as mercury and can form strong bonds with these heavy metals. Weak correlations were also observed in the present study between CEC and mercury concentrations in paddy fields ( $R^2=0.21$ ,  $p<0.05$ ) and in dry fields ( $R^2=0.23$ ,  $p<0.05$ ) (Fig. 4c, f). Higher soil



**Fig. 4** Relationships between soil physicochemical properties and mercury concentrations. **a–c** Physicochemical properties of paddy fields, **d–f** physicochemical properties of dry fields

CEC provides more anion sites for mercury adsorption, resulting in greater adsorption of mercury into soils over time (Soares et al., 2015).

The differences in soil pH and CEC between paddy fields and dry fields were not significant, but the organic matter content of the paddy fields was much higher than that of the dry fields (Table 3); therefore, soil organic matter may be one of the factors contributing to the clear differences in mercury concentrations between paddy fields and dry fields in mercury mining areas. Hissler and Probst (2006) investigated the relationship between soil organic carbon and mercury concentrations, and the results showed that mercury was more enriched in organic matter-rich soil layers. Decreased oxidation of paddy field soil can reduce the decomposition rate of organic matter compared to soil in dry fields, leading to accumulation of organic matter (Sahrawat, 2004). Organic matter can increase sorption of mercury by altering the pH, CEC, and other physicochemical properties of the soil (Wang et al., 2014). It has also been reported that for paddy fields, flooding facilitates leaching of dissolved organic matter, which contains numerous acidic functional groups, such as carboxyl, phenolic hydroxyl, amine, alcohol hydroxyl, and thiol. Mercury ions preferentially bind to these acidic functional groups, which in turn bind to thiol and other sulfur-containing functional groups, producing a stable bound state in the paddy field system (Ravichandran, 2004). This may explain the high mercury concentrations in paddy fields.

## Environmental risk assessment

### *Ecological risk assessment*

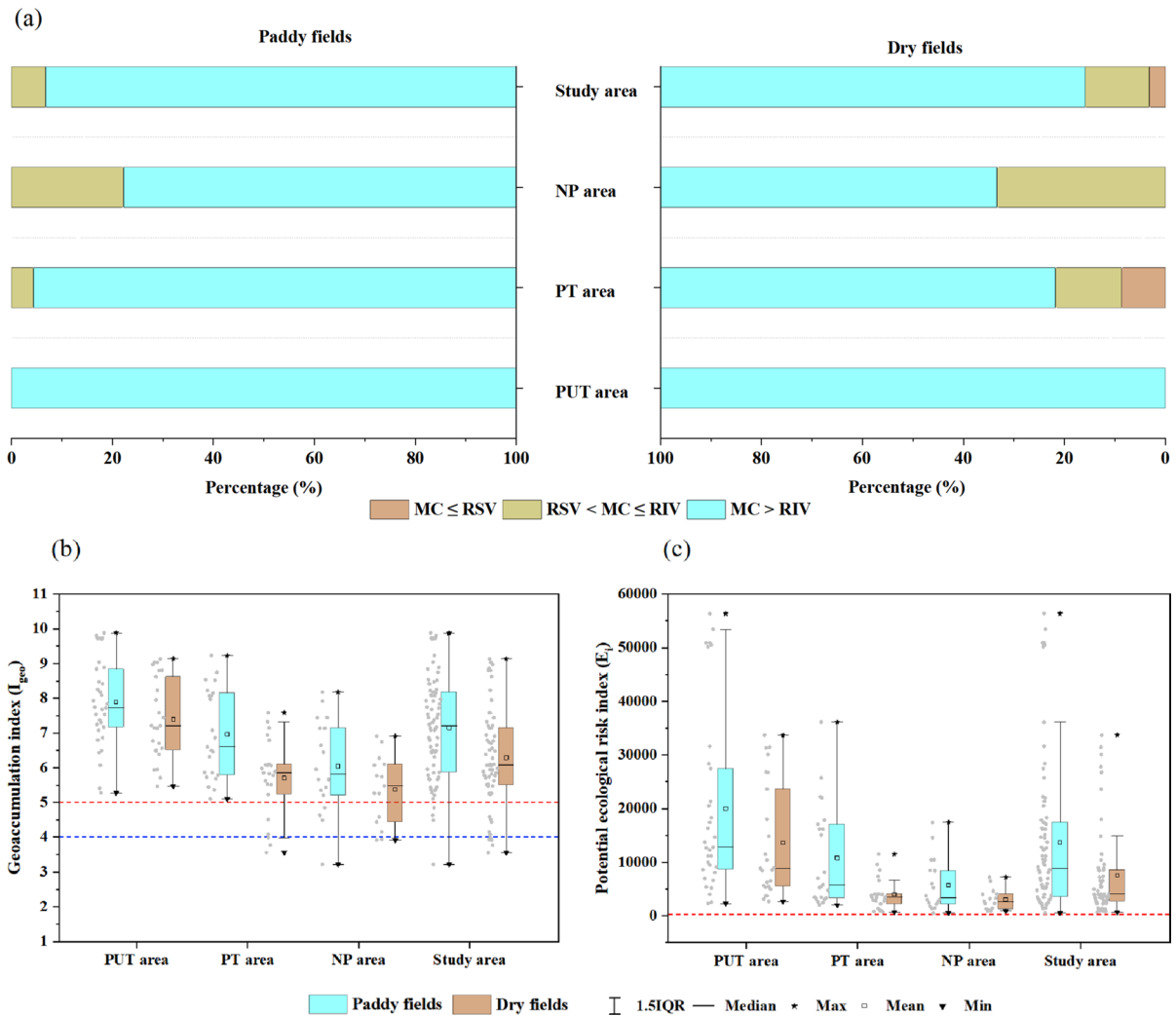
Compared to the soil pollution risk control standards for agricultural land (MEE, 2018) (Fig. 5a), all of the paddy field samples exceeded the risk screening value; only 6.76% of the paddy field samples were below the risk intervention value and 93.24% of the paddy field samples exceeded the risk intervention value. Similarly, only 3.17% of the dry field samples were below the risk screening value; 15.78% of the dry field samples were below the risk intervention value and 84.13% of the dry field samples exceeded the risk intervention value. In the PUT area, 100.00% of the paddy field samples and 100.00% of the dry

field samples exceeded the risk intervention value, so the farmland in the PUT area belongs to the strict control category. In the PT area, 95.65% of paddy field samples exceeded the risk intervention value, while only 78.26% of dry field samples exceeded the risk intervention value; the reasons for this difference require further exploration. In the NP area, 77.78% of the paddy field samples and 66.67% of the dry field samples exceeded the risk intervention value, meaning that only a small portion of the farmland may be safely cultivated in this area. The paddy fields and dry fields in the study area generally belongs to the strict control category, consistent with the results of Zhu et al (2021). Therefore, there is an urgent need for synergistic monitoring and assessment of soil and crops in the study area, as well as for a number of other risk management measures, such as conversion of farmland to other uses.

The geoaccumulation index ( $I_{geo}$ ) mainly emphasizes the level of enrichment in heavy metal concentrations based on the geological background. The potential ecological risk ( $E_i$ ) not only considers the nature of the heavy metals and transport in the environment, but also takes into account toxicity (Kowalska et al., 2018; Zhang et al., 2021). The mercury concentrations in the agricultural soils were evaluated using these indexes (Fig. 5b and c). The average values of  $I_{geo}$  for the paddy fields and dry fields in the study area were 7.15 and 6.29, respectively, indicating that the pollution level in agricultural soils was extremely high. The geoaccumulation indexes for the three areas were in the order PUT > PT > NP; and the pollution levels in the paddy fields and dry fields in all areas were extremely high. The average values of  $E_i$  for the paddy fields and dry fields in the study area were 13,684 and 7556, respectively, indicating that the ecological risk of the agricultural soils was also extremely high. In terms of potential ecological risk indexes for the three areas, PUT > PT > NP, and the ecological risks in the paddy fields and dry fields in all areas were extremely high. In conclusion, the level of soil pollution and the ecological risks associated with agricultural soils in the study area need attention.

### *Health risk assessment*

The heavy metals that accumulate in the edible parts of the crops are ingested by consumers; they



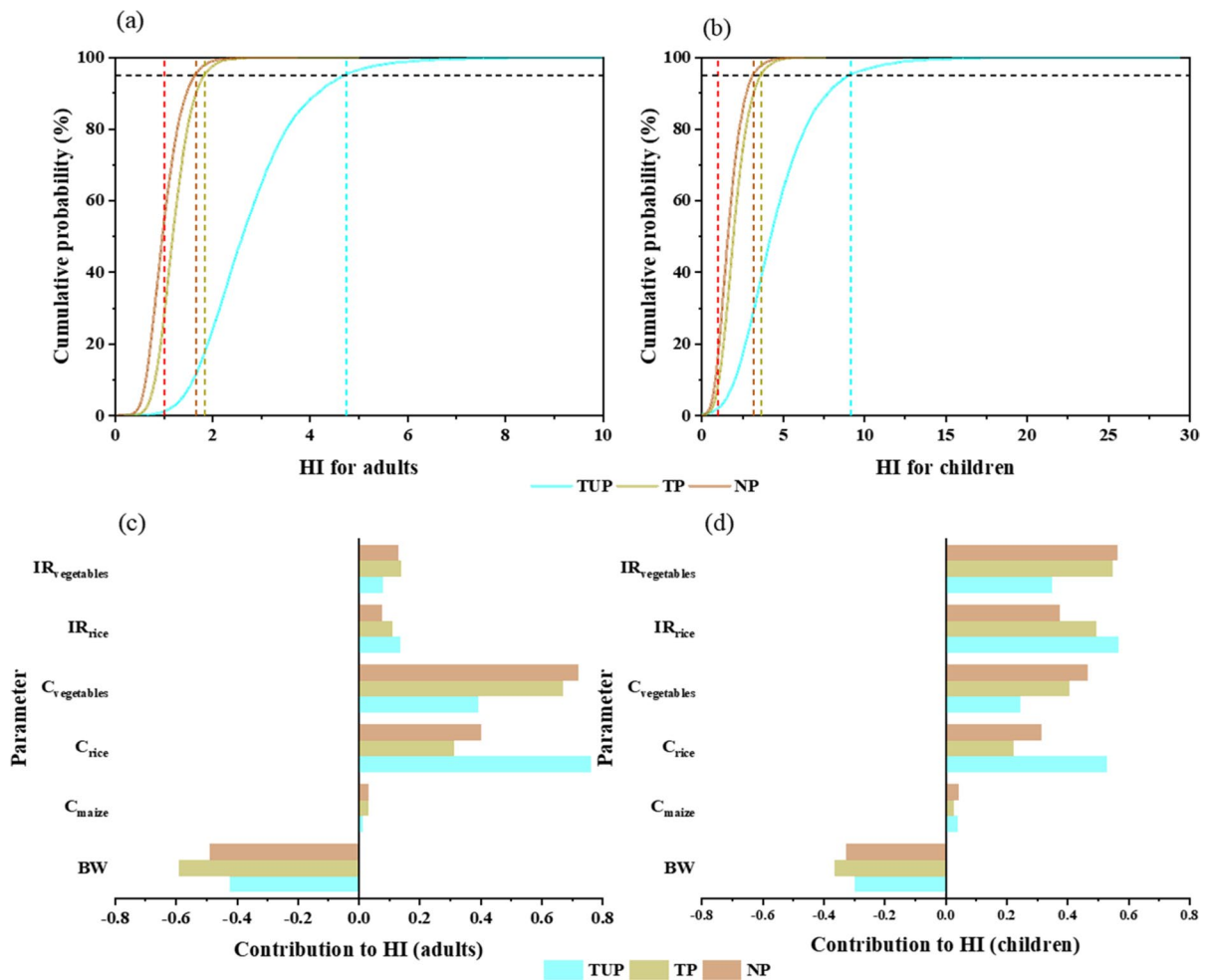
**Fig. 5** Soil pollution and ecological risk evaluation. **a** Compared to the soil pollution risk control standards for agricultural land, MC is the mercury concentration in agricultural soil, RSV is the risk screening value, and RIV is the risk intervention value (based on the soil pH, the RSV for the paddy fields is 1.0 mg/kg, the RIV for the paddy fields is 6.0 mg/

kg; the RSV for the dry fields is 2.4 mg/kg, and the RIV for the dry fields is 4.0 mg/kg). **b** Geoaccumulation index: the red dashed line is the extremely high level and the blue dashed line is the high to extremely high level. **c** Potential ecological risk index: the red dashed line is the extremely high level

gradually accumulate in various tissues and organs of the human body and eventually affect human health (Khanam et al., 2020; Zakaria et al., 2021). Therefore, the human health risk assessment model was used to compare the average daily intake of mercury from each crop by local adults and children with the daily allowable intake of mercury. The FAO/WHO provisional tolerable weekly intake (PTWI) values for mercury are 1.6 µg/kg-week for children and 3.3 µg/kg-week for adults (FAO/WHO, 2007). The

probabilistic risk assessment (Fig. 6a and b) showed that the 95th percentile of total hazard quotients(HI) for adults were 4.74, 1.83, and 1.65 in the PUT, PT and NP areas, respectively, and the 95th percentile of total hazard quotients(HI) for children were 9.17, 3.65, and 3.17 in these areas, respectively. The HI for consumption of vegetables, mushrooms and fish by adults of mercury mining area in Spain was 4.87 (Jimenez-Oyola et al., 2020); the HI for consumption of rice, corn, vegetables, and other food





**Fig. 6** Health risk assessment of local residents' consumption of crops. The black dashed line is the 95th percentile; the red dashed line is the total hazard quotient of 1; the orange dashed line, the yellow dashed line and the blue dashed line are the 95th percentile of the HI for the three areas respectively; **a**

probabilistic risk analysis of HI for adults in three areas, **b** probabilistic risk analysis of HI for children in three areas, **c** sensitivity analysis of all parameters in adults, **d** sensitivity analysis of all parameters in children

by adults of Wanshan mercury mining area was 2.23 (Xu et al., 2020). These results indicate unacceptable health risks from mercury intake to the local residents through consumption of crops. The HI for children was 1.92–1.99 times higher than that for adults in the same area, indicating that children are more likely to be harmed than adults in mercury mining areas. Furthermore, the risks to human health in the PT area were similar to those in the NP area, likely due to the completed treatment of mercury slag piles surrounding the PT area. If the same treatment measures were applied to the mercury slag piles surrounding the PUT area, the HI of local adults and children

would likely be decreased by 47.06% and 79.90%, respectively.

Sensitivity analysis was performed to identify the impacts of uncertain parameters and the most significant parameters associated with health risk (Fig. 6c and d). Mercury concentrations in vegetables ( $C_{vegetables}$ ), mercury concentrations in rice ( $C_{rice}$ ), and body weight (BW) were found to be the most significant parameters affecting the results of the adult health risk assessment. The rice mercury concentration in the PUT area was significantly higher than in the other areas, resulting in a contribution of 76.23% by  $C_{rice}$ ; however, in the NP area, rice mercury

concentrations were lower than those of vegetables, resulting in a contribution of 72.09% by  $C_{\text{vegetables}}$ . The average daily intake of vegetables ( $IR_{\text{vegetables}}$ ), average daily intake of rice ( $IR_{\text{rice}}$ ), mercury concentrations in vegetables ( $C_{\text{vegetables}}$ ), mercury concentrations in rice ( $C_{\text{rice}}$ ), and body weight (BW) were the most significant parameters affecting the results of the children health risk assessment. It was also found that the contribution of body weight (BW) to HI was negative, indicating that the weight increased and the health risk decreased, which is consistent with the research results of Jafarzadeh et al. (2022) and Cheng et al. (2023).

In addition, maize is a local and seasonal staple food and local exposure parameters are not easily available (Xu et al., 2020), which makes it difficult to accurately estimate the health risks associated with consumption of maize. However, due to the high concentrations of mercury in maize in the study area, it should be included in future health risk assessment.

## Conclusion

This study showed that pollution from large mercury slag piles cannot be overlooked. By investigating the agricultural soils and crops in the Tongren mercury mining area, it was found to be seriously polluted, and the trend of pollution was  $PUT > PT > NP$ . The mercury concentration in paddy fields ( $37.63 \pm 37.96$  mg/kg) was higher than that in dry fields ( $20.78 \pm 22.67$  mg/kg). The mercury concentrations in local rice, maize and vegetables all exceeded Chinese food safety limits. The mercury accumulation factors for rice, maize, pepper, eggplant, tomato and bean were  $1.2 \times 10^{-3}$ ,  $4.0 \times 10^{-4}$ ,  $1.4 \times 10^{-3}$ ,  $2.9 \times 10^{-3}$ ,  $2.1 \times 10^{-3}$  and  $2.5 \times 10^{-3}$ , respectively; the accumulation capacity was influenced by plant species and may be unrelated to the planting environment. The main pathways for residual mercury from the waste residues to enter the agricultural land were atmospheric deposition, agricultural irrigation and rainfall runoff; and higher organic matter may influence the soil to adsorb more mercury. Soil pollution levels and potential ecological risks were extremely high in all agricultural areas, so the management and use of these agricultural lands need to be taken into account. Assessment of the health risks associated with the ingestion of mercury from these crops

by local residents revealed that the 95th percentiles of  $HI > 1$ , suggesting that the health risks were unacceptable for all areas.

In addition, this study found that if the same measures were applied to the untreated slag pile compared to the treated area, it would decrease mercury concentrations in agricultural land, further it may decrease the health risks of residents. Therefore, it is recommended that large mercury slag piles be treated as early as possible to decrease the environmental risk of mercury in the waste residues into surrounding environmental media.

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**Author contributions** CZ contributed to data curation, formal analysis, visualization and writing; TX and LZ were involved in conceptualization, methodology, writing–review& editing, funding acquisition; ZC and HZ collected all samples; XJ, LJ and XZ completed the English editing during the preparation of this manuscript; GL provided historical information about the study area. All authors reviewed the manuscript.

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## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that would influence the work reported in this paper.

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