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Cadmium contamination in a soil-rice system and the associated health risk: An addressing concern caused by barium mining

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ABSTRACT

Cadmium (Cd) is associated with barite; however, its biogeochemical characteristics in environments impacted by barium (Ba) mining are not known. Here, we first revealed the characteristics of Cd concentrations, distributions, and chemical forms in the soil-rice system in Ba mining areas. The associated exposure and risk assessments of Cd via rice consumption were also conducted. Elevated levels of Cd with a wide range of 0.054–91 mg/kg were found in paddy soils, approximately 63% of which exceeded the national Grade II value for soil Cd levels in China (0.3 mg/kg). A significant positive correlation between the soil Cd and soil Ba demonstrated that large amounts of Cd were released into the environment from Ba mining. Cadmium accumulated remarkably in the rice grains (0.007–3.5 mg/kg). The chemical forms in the rice plants indicated that most of the Cd was in the pectate/protein fraction (F2, 92% in the grains and 61–71% in the other tissues), followed by the residual fraction (F3, 7.1% in the grains, 27–38% in the other tissues). A minor portion of Cd was in the soluble and aminophenol fraction (F1, 0.44% in the grains, 0.26–1.4% in the other tissues). The positive correlations observed between the grain Cd and F2 in the roots, stems and leaves suggested that Cd in the rice grain was mainly from F2. Similarly, the root F2 was also positively correlated with that in the stems/leaves, indicating the critical role of F2 in Cd^{2+} migration in rice tissues. The estimated average hazard quotient (2.5) and annual excess lifetime cancer risk (21×10^{-5} a^{-1}) were higher than the safety levels of 1 and 5.0×10^{-5} a^{-1}, respectively, showing that the dietary intake of Cd via rice consumption posed high health risks to residents. Our study demonstrated that more concerns should be paid to Cd contamination in Ba mining areas.

1. Introduction

Cadmium (Cd) is a toxic element and is classified as a group 1 carcinogen that is associated with lung, breast and bladder cancer (Nordberg, 2009). The toxin can be retained in the kidneys for as long as 10–30 years (Clemens et al., 2013), resulting in renal failure and osteopenia due to its high binding affinity to proteins, amino acids, enzymes and symports (Jarup and Akesson, 2009). Increasing epidemiological studies have indicated that Cd exposure may also cause other adverse effects, such as gestational diabetes mellitus (Xing et al., 2018). Recent investigations have demonstrated that even at low levels of exposure, Cd causes risks to human health (Mezynska and Brzoska, 2018).

Cadmium can be readily absorbed by plants and is found in most foodstuffs (Chen et al., 2018). Rice is a significant source of Cd intake. The notorious itai-itai disease that occurred in Japan was caused by the intake of Cd-contaminated rice (Jarup and Akesson, 2009). In plants, Cd exists in various chemical forms that are highly related to their migration behaviors (Wu et al., 2005). Lai (2015) studied the chemical form of Cd in Impatiens and found that most of the Cd was in the pectate- and protein-integrated forms, which exhibited high mobility of translocation from roots to shoots. Studies on rice under hydroponic conditions suggested that ethanol- and sodium chloride-extractable Cd were predominant in tissues (He et al., 2008; Zhang et al., 2014). Similar results were reported by Luo et al. (2017), who also observed that ethanol and deionized water-extractable Cd was positively correlated

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with grain Cd levels. However, little information about the distributions and migration processes of different Cd chemical forms in the tissues of rice growing under field conditions is available.

Since Cd is a dispersed element, it has difficulty becoming enriched and mineralized and is usually associated with zinc (Zn) and lead (Pb) ores (Kabata-Pendias, 2011). The major anthropogenic Cd source in the environment is Zn/Pb ores (Garrett, 2000). However, barium (Ba) ore (mostly in barite ($BaSO_4$)) was found to enrich Cd. Trefry et al. (1986) and Crecelius et al. (2007) reported concentrations as high as 9.9 mg/kg and 7 mg/kg Cd in barite, respectively. Recently, Shahab et al. (2016) found that the Cd concentration in barite ore was as high as 30.9 mg/kg. High concentrations of Cd in barite suggest that barite is an important source of Cd in the environment. Currently, little information on the environmental impact of the Cd associated with Ba mining is available.

China is rich in barite ($BaSO_4$), and its reserve ranks first in the world, reaching approximately 600 million tons (Li, 2004). Because of its abundant Ba ores, China became the world's largest Ba-producing country, and the average annual barite production was 4.02 million tons during 2007 and 2011, representing 50% of global production (Johnson et al., 2017). Intensive Ba mining activities and the related manufacturing of chemical compounds occur in the world's largest Ba mine, the Tianzhu Ba mine in Guizhou Province, Southwest China; this mine is expected to be the most likely origin for not only Ba but also Cd in the environment, which provides an excellent opportunity to verify the hypothesis that Ba mining is an important source of Cd. A better understanding of Cd biogeochemical process is crucial for reducing exposure risk in Ba mining regions.

In the present study, the concentration, distribution, and speciation of Cd in a soil-rice system in the region of the Tianzhu Ba mine was elucidated to delineate the linkage between Cd contamination and Ba mining. The migration of different chemical forms of Cd in rice tissues was revealed. Finally, the health risks to local populations consuming rice with elevated Cd levels was evaluated.

2. Materials and methods

2.1. Study area

Tianzhu is located in eastern Guizhou Province, Southwest China. The area has a subtropical humid monsoon climate. The annual average precipitation is 1280 mm, and the average annual temperature is 16 °C. The major river is the Jianjiang River, with the Mibei, Langjiang, and Fuluo Rivers as its tributaries. The population of this county was 0.43 million in 2016. Rice is the main cereal crop, with a planting area reaching 22,175 ha in 2016.

Tianzhu is the largest Ba mine and Ba salt manufacturing area and is called the "land of barite" in China. Ba mining activities began in the 1950s. The ore-forming materials are mainly derived from seawater and hydrothermal sedimentation (Hou et al., 2015). The gangue minerals in Tianzhu are mostly quartz, barite and minor amounts of calcite, bitumen and hydrothermal apatite (Wen et al., 2017). During the mining process, large amounts of barite ore ($BaSO_4$) was piled on the ground, which is shown in Fig. S1. Those ores not stored under controlled conditions might result in harmful elements being released into the surrounding area under natural weathering conditions.

2.2. Sample collection and preparation

A total of 82 samples of paddy soils and paired rice plants were collected during the rice harvest season in 2017 (Fig. 1). Briefly, soil samples were taken from the rice rhizosphere after removing the covering materials (e.g., leaves, stones) and placed into clean polyethylene bags to avoid cross-contamination. The samples were labeled and transported to the laboratory. Then, the soils were freeze-dried, ground with a mortar and pestle, and filtered with a 200-mesh sieve. Gravel and plant residues were removed before grinding. The powder samples were stored in sealed clean polyethylene bags prior to digestion.

The rice plants were cleaned with drinking water and separated into roots, stems, leaves and grains in situ. All samples were placed in clean polyethylene bags to avoid cross-contamination. In the laboratory, the rice tissue samples were further washed with ultrapure water and freeze-dried (EYELA model FDU-1100, Japan). The rice grains were further separated into hulls, bran, and polished parts (white rice) and then ground with a 150-mesh (IKA-A11; IKA, Germany) prior to analysis.

2.3. Sample analysis

2.3.1. Soil

Approximately 0.05 g of soil sample was acid-digested in a Teflon crucible with a mixture of concentrated HNO_3 (3 mL) and HF (1 mL) in an oven at 160 °C for 48 h. Then, HNO_3 (1 mL) was added to the Teflon crucible and heated until complete evaporation of the solution occurred. Then, deionized water (2 mL) and HNO_3 (3 mL) were added to dissolve any residues. The digestion solution was transferred to a 15 mL centrifuge tube. Approximately 2 mL of the diluted digestion solution was measured by TAS 990 graphite furnace atomic absorption spectrometry (GFAAS, Puxi, Beijing, China).

2.3.2. Rice grains

Approximately 0.2 g of white rice was placed into a Teflon crucible with 3 mL of HNO_3. Then, the crucible was sealed in a stainless-steel container and heated in an oven at 150 °C for 6 h. After the digestion solution cooled, 2 mL of H_2O_2 was added and heated until complete evaporation of the solution occurred. Deionized water (3 mL) and HNO_3 (2 mL) were added to the Teflon crucible for another 5 h of digestion. The digestion solution was transferred to a 15 mL centrifuge tube. Approximately 2 mL of the diluted digestion solution was measured by GFAAS, similar to the soil Cd measurement.

2.3.3. Chemical forms of Cd in the rice tissues

The extraction of three Cd chemical forms in the roots, stems, leaves, and grains of the rice plant samples (n = 13) was conducted. The chemical forms of Cd were extracted sequentially according to Wu et al. (2012) and Xue et al. (2018). Briefly, the soluble and aminophenol Cd (F1) was extracted with 80% ethanol; the insoluble $CdHPO_4$, $Cd_3(PO_4)_2$, and other Cd-phosphate complexes as well as Cd integrated with pectates and proteins (F2) were extracted with 0.6 M HCl; the residual portion (F3) was extracted with HNO_3–H_2O_2.

2.4. Health risk assessment

2.4.1. Calculation of estimated weekly intake

To determine the Cd exposure through rice, the estimated weekly intake (*EWI*) of Cd in this study was calculated using the following equation:

$$EWI = (C \times WC)/BW$$

where.

EWI Estimated weekly intake of Cd (mg/kg BW/week)
C Concentration of Cd in rice (mg/kg)
WC Weekly intake of rice (kg/week) (WC = 0.392 kg/day × 7; Zhao et al., 2017)
BW Average body weight (kg) (BW = 60 kg; BGS (Bureau of Guizhou Statistics), 2007)

2.4.2. Calculation of noncarcinogenic and carcinogenic risks

The health risk assessment models recommended by the US Environment Protection Agency (EPA) were applied to assess both the noncarcinogenic and carcinogenic effects of Cd in this study (USEPA,

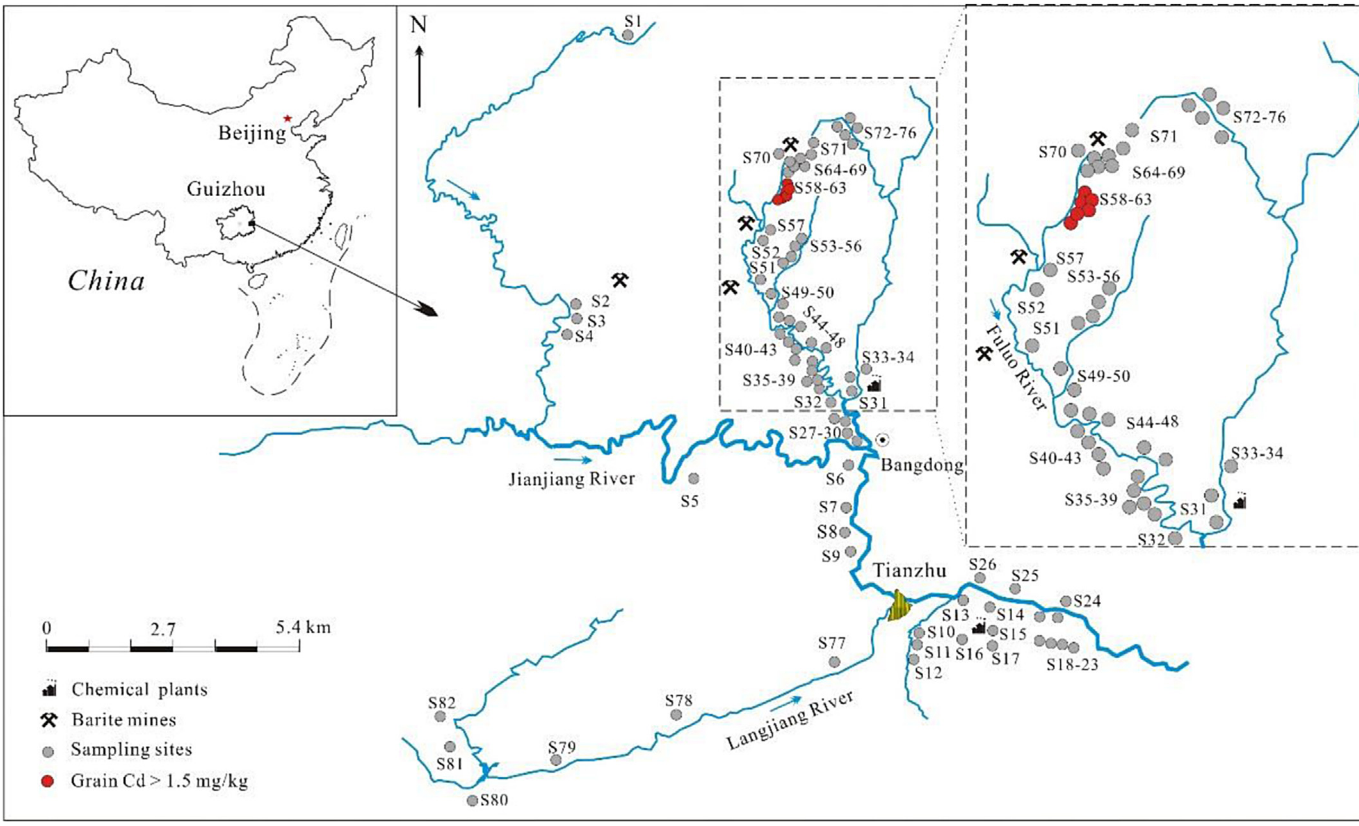

Fig. 1. Map of sampling sites.

1997). The noncarcinogenic risk was calculated as follows:

$$EDI = EWI/7$$

$$HQ = EDI/RfD$$

where.

EDI Estimated daily intake of Cd (mg/kg BW/day)
HQ Hazard quotient
RfD Oral reference dose for Cd (mg/kg BW/day) ($RfD = 0.001$ mg/kg BW/day; USEPA, 2015)

The potential carcinogenic risk through rice Cd exposure was calculated as follows:

$$AELCR = \frac{1 - exp(-EDI \times SF)}{DL}$$

where.

AELCR The annual excess lifetime cancer risk
SF The slope factor of Cd for carcinogenic effects (kg BW. day/mg)
DL The average human longevity

Among these, *SF* was 6.1 kg BW day/mg, which was recommended by the Integrated Risk Information System (USEPA, 1985), and *DL* was chosen as 70, which was recommended by Yuan et al. (2014).

In this study, in addition to the deterministic risk assessment using the above formulas, the Monte Carlo simulation technique with 10,000 iterations was conducted via Crystal Ball software (version 11.1.2.4, Oracle Co. ltd, USA) for the probabilistic risk assessment. The upper 95% confidence interval ($P_{95\%}$) was chosen to derive the conclusion about the presence or absence of the health risk (Koupaie and Eskicioglu, 2015).

2.4.3. Calculation of the predicted urinary Cd

A one-compartment toxicokinetic model was used to predict the urinary Cd (U–Cd) level of the population in the current study area. The predicted U–Cd level was calculated as follows:

$$Cd_{urine}(age) = \frac{f_u \times f_k}{log(2)} \times d \times t_{1/2} \frac{\left[1 - exp\left(-\frac{\log(2)\times age}{t_{1/2}}\right)\right]}{\left[1 - exp\left(-\frac{\log(2)}{t_{1/2}}\right)\right]}$$

where.

f_u Ratio between Cd in the urine and in the kidney cortex
f_k A factor aggregating several physiological and Cd-related constants
d Cd intake
$t_{1/2}$ Cd half-life

The statistical estimates of the model parameters were 0.005 and 11.6 for $f_u \times f_k$ and $t_{1/2}$, respectively (Amzal et al., 2009). The age of 50 years was chosen in the calculation (WHO, 2004). Rice is the most important source of Cd exposure for nonsmokers in China (Zhao et al., 2017). Hence, *d* represented Cd intake through rice in this study.

2.5. QA/QC

Duplicates, method blanks and certified reference materials (GSS-5; GBW10020) were used for quality assurance and quality control. The relative difference in Cd between duplicate soil samples was < 4.3% and < 5.0% in the rice samples. For the yellow red soil reference material (GSS-5), the recoveries ranged from 83% to 101%. The Cd concentration in the citrus leaf reference material (GBW 10020) was measured, with recoveries ranging from 84% to 99%. During the analysis process, a Cd standard stock solution of 0.5 ng/mL was measured

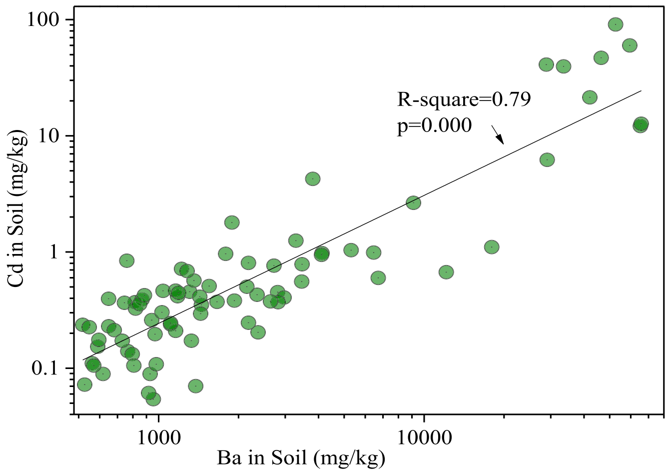

Fig. 2. The relationship between the soil Ba and soil Cd concentrations.

for every 15 samples, and the recoveries ranged from 85% to 96%.

3. Results and discussion

3.1. Cd concentrations

3.1.1. Paddy soil

The Cd concentrations in the soil samples ranged widely, from 0.054 to 91 mg/kg, with an average value of 4.5 mg/kg. Samples S58, S59, S61, S62, and S63, which were impacted by barite ore ($BaSO_4$), exhibited relatively high Cd concentrations. The Cd concentrations exceeded the average Chinese farmland value (0.24 mg/kg; Huang et al., 2019). Approximately 63% of the samples exhibited Cd concentrations greater than the national Grade II value of 0.3 mg/kg Cd for soils in China, and the highest value was approximately 2 orders of magnitude higher (Ministry of Environment Protection of the People's Republic of China, 1995). Generally, elevated levels of Cd were observed in the Ba-contaminated paddy soils. We found a significantly positive correlation (R-square = 0.79, p = 0.000) between the concentrations of soil Cd and soil Ba (Fig. 2). Soil Cd was positively correlated with soil Ba, which might indicate that barite ($BaSO_4$) is an important source of Cd.

Severe Cd contamination was observed in the soils surrounding Pb–Zn mines (Lei et al., 2010; Huang et al., 2017). Our results for the Cd concentrations in soils were comparable to those reported by previous investigations on Pb–Zn mines in China and higher than those found in other countries (Table 1). The elevated levels of Cd as well as its significant positive correlation with soil Ba in the barite mining areas confirmed that Ba mining is an important Cd source. Much attention should be paid to the release of Cd from barite mining, which is crucial for assessing Cd cycles in the environment.

3.1.2. Rice grains

The rice grain showed a great ability to accumulate Cd. Compared to those in other cereals, the Cd concentration in the rice grains was 3–8 times higher (Song et al., 2017). The elevated concentrations of Cd in rice may be attributed to its expression levels of the *OsNramp5* and Nramp5 proteins, which were higher than those observed in other cereals (Sui et al., 2018).

In the present study, the concentrations of Cd in rice grains ranged widely, from 0.007 to 3.5 mg/kg, with an average value of 0.38 mg/kg. Almost all of the high Cd concentration rice samples were collected from sites with high concentrations of soil Cd, such as S58, S59, S60, S61, S62, and S63. The significant positive correlation between rice Cd and soil Cd is shown in Fig. S2 (R-square = 0.56, P = 0.000), indicating that soil Cd is a dominant source of rice Cd.

Approximately 37% of the samples exhibited rice Cd concentrations greater than the maximum permissible value for Cd in rice in China (0.2 mg/kg; Ministry of Health of the People's Republic of China, 2017), and the highest value (3.5 mg/kg) was approximately 20 times higher than the maximum permissible value. Compared with the values observed in certain polluted regions, such as a nonferrous metal processing area, an electronic waste site and a Cd-containing industrial wastewater irrigation region in China, the rice Cd concentration in the study area was significantly higher (Table 2). Our results suggest that serious Cd contamination occurred in the rice. The elevated levels of Cd in the rice grains suggest that the Cd released from Ba mining is bioavailable and ready for uptake and accumulation in grains.

3.2. Chemical forms and potential migration of Cd in the rice tissues

3.2.1. Chemical forms of Cd in the rice tissues

The Cd in the grains was predominately in the pectate/protein form, F2 (extracted with 0.6 M HCl), accounting for 92% of the total amount of Cd that accumulated, followed by the residual portion, F3 (extracted with HNO_3–H_2O_2), and F1 (extracted with ethanol), accounting for 7.1% and 0.44%, respectively (Fig. 3a). Similar trends were also found in the roots, stems and leaves (Fig. 3b–d). F2 was the major Cd form (61–71%), followed by F3 (27–38%) and F1 (0.26–1.4%). The largest amounts of Cd were in the F2 form in the rice tissues, which was in agreement with the results reported by Huo et al. (2016) and similar to the results for radish cultivars (a Cd-tolerant genotype and a Cd-sensitive genotype), Impatiens, duckweed, and *Brassica napus* (Lu et al., 2015; Mwamba et al., 2016; Xin et al., 2017; Xue et al., 2018).

This phenomenon might be attributed to the numerous coordination sites on the surface of proteins, which leads to a potential Cd^{2+} binding capacity (Feng et al., 2019). Kato et al. (2010) found that the Cd present in rice phloem sap may bind to a novel protein weighing approximately

Table 1
Comparison of the Cd concentrations in soils near the Ba mine area in this study and previous investigations in soils surrounding Pb–Zn mines (mg/kg).

Region	Country	Mine type	N	Min	Max	Average value	Reference
Tianzhu	China	Ba mine	82	0.054	91	4.5	This study
Kocani	Macedonia	Pb–Zn mine	38	0.1	6.4	0.9	Dolenec et al. (2007)
Abakaliki	Nigeria	Pb–Zn mine	12	0.24	5.33	1.62	Nnabo, 2015
Kirki	Greece	Pb–Zn mine	16	0.2	7.5	1.93	Nikolaidis et al. (2013)
Ciudad Real	Spain	Pb–Zn mine	9	n.d.	4.89	2.47	Rodríguez et al. (2009)
Suxian	China	Pb–Zn mine	87	0.35	6.47	2.94	Song et al. (2015)
Guiyan	China	Pb–Zn mine	163	1.5	11.5	3.4	Lu et al. (2015)
Yangshuo	China	Pb–Zn mine	10	0.47	11.2	4.82	Cao et al. (2018)
Shaoguan	China	Pb–Zn mine	455	< 0.02	95.4	5.16	Zhou et al. (2015)
Chenzhou	China	Pb–Zn mine	83	0.01	114.73	6.13	Huang et al. (2017)
Huize	China	Pb–Zn mine	496	0.213	108.83	7.27	Wu et al. (2018)
Chenzhou	China	Pb–Zn mine	/	/	/	11.9	Lei et al. (2010)

"n.d." is less than the detection limit.
"/" is no data available.

Table 2
Comparison of the Cd concentrations in the rice grains in the current study area and those in other polluted areas in China (mg/kg).

Region	Province	Growth area	N	Average value	Minimum	Maximum	Reference
Tianzhu	Guizhou	Barium mining district	82	0.38	0.007	3.5	This study
Chenzhou	Hunan	Polymetallic mining district	27	0.24	/	/	Zhai et al. (2008)
Yiyang	Hunan	Gold mining district	10	0.3	/	/	Williams et al. (2009)
Taizhou	Zhejiang	Electronic waste recycling	13	0.22	0.012	0.661	Fu et al. (2008)
Shenyang	Liaoning	Wastewater irrigation region	97	0.166	0.011	1.167	Ke et al. (2015b)
Gejiu	Yunan	Nonferrous metal processing activities	96	0.16	0.01	0.639	Ke et al. (2015b)
Shaoguan	Guangdong	Polymetallic mining district	99	0.157	0.018	0.498	Ke et al. (2015b)
Hezhang	Guizhou	Indigenous zinc-smelting activities	95	0.189	0.023	0.487	Ke et al. (2015b)
Weiling	Zhejiang	Electronic waste recycling	96	0.072	0.002	0.469	Zhao et al. (2010)
Shengzhou	Zhejiang	Highly industrialized areas	15	0.07	0.00	0.2	Zhao et al. (2009)
Zhengzhou	Henan	Municipal sewage irrigation region	15	0.016	0.014	0.22	Liu et al. (2007)

"/" is no data available.

13 kDa. In addition, metal chemical forms highly reflect their toxicity to plants. It has been recognized that Cd bound to proteins/pectates exhibits lower deleterious effects on plant cells than Cd in inorganic and water-soluble forms (Xu et al., 2011). Wu et al. (2005) demonstrated that Cd-sensitive barley cultivars had lower concentrations of pectate/protein-integrated Cd and higher concentrations of water-soluble and inorganic Cd than those detected in Cd-resistant cultivars. Hence, it might be possible to alleviate Cd toxicity by binding large amounts of Cd to pectates/proteins in rice plants.

3.2.2. *Potential migration of the Cd chemical forms among rice tissues*

The processes for Cd accumulation in rice grains depend on root uptake, translocation to shoots, redirection at nodes, and remobilization from leaves (Uraguchi and Fujiwara, 2013). Additionally, Cd^{2+} migration behaviors are highly related to its chemical forms (Chavez et al., 2016). Xie et al. (2018) observed significantly positive correlations of the Cd concentrations between rice grains and tissues. However, little information is available about the role of the chemical forms in the migration processes of Cd^{2+} among rice tissues.

Among the three chemical forms, the roots, stems, and leaves exhibited a more positive correlation with the grains in the F2 form than in the F3 and F1 forms (Fig. 4a–f; Figs. S3a–c), suggesting that the protein/pectate-bound Cd compounds had a greater contribution to the grain Cd^{2+} levels. Xue et al. (2018) reported that F2 and F1 played a dominant role in Cd transfer within a duck-tilapia food chain and that F1 played a key role. However, in the present study, F1 in the roots, stems, and leaves did not display a strong correlation with the grain Cd^{2+} levels. It might be possible that the transmission of Cd^{2+} in the food chain is different from the processes in plant systems. Further research is needed to determine the transport mechanism of F2 from other tissues of rice into the grains.

The correlation between the stem/leaf Cd^{2+} concentrations and the chemical forms of Cd in roots is displayed in Fig. 4g–h and Fig. S3d. A strong correlation was obtained between the leaf Cd^{2+} and root F2 levels (R-square = 0.91), followed by the stem Cd^{2+} and root F2 levels (R-square = 0.80), leaf Cd^{2+} and root F3 levels (R-square = 0.78), and stem Cd^{2+} and root F3 levels (R-square = 0.76), whereas no significant correlation between the stem/leaf Cd^{2+} and root F1 levels was observed. The results indicated that the Cd chemical forms played an important role in the transfer of Cd^{2+} from the roots to the stems and leaves. Lai (2015) reported that the root Cd concentration in the protein/pectate forms exhibited a positive linear relationship with the shoot Cd concentration, and the linear regression equation established predicted the shoot Cd concentration in Impatiens. Similarly, Gong et al. (2003) proposed that Cd^{2+} in the roots of *Arabidopsis* was transported to the shoots through PCs–Cd^{2+} (phytochelatins chelate Cd^{2+}), which decreased the toxic effects of Cd^{2+}. Furthermore, a recent study reported that the defensin-like protein CAL1 (Cd accumulation in leaf 1) might specifically chelate Cd in the cytosol, facilitating Cd secretion to extracellular spaces to promote Cd translocation from roots to shoots (Luo et al., 2018). These studies suggest that Cd-binding proteins play a key role in the migration process among rice tissues.

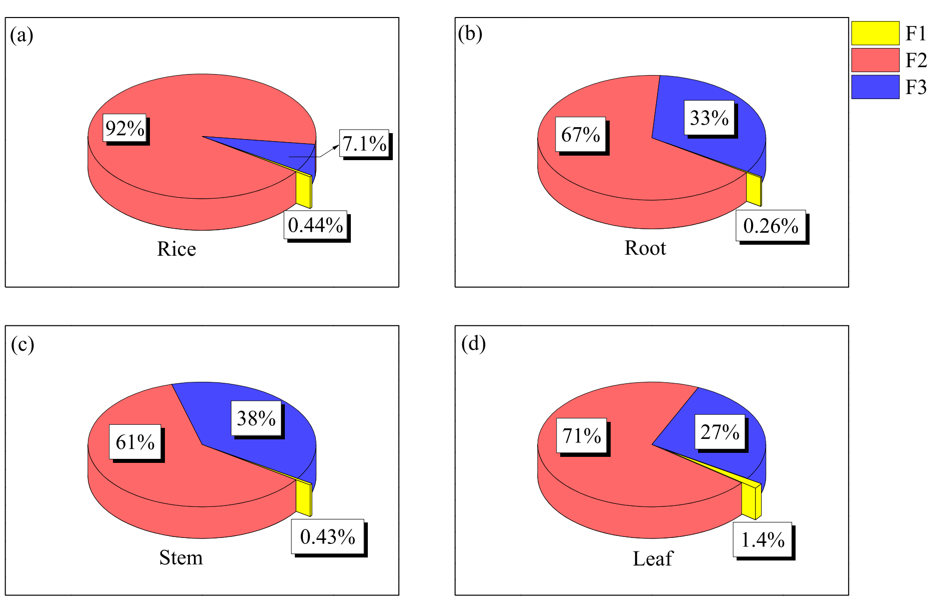

Fig. 3. Percentage of each Cd chemical form in the rice grains, roots, stems and leaves of rice plants.

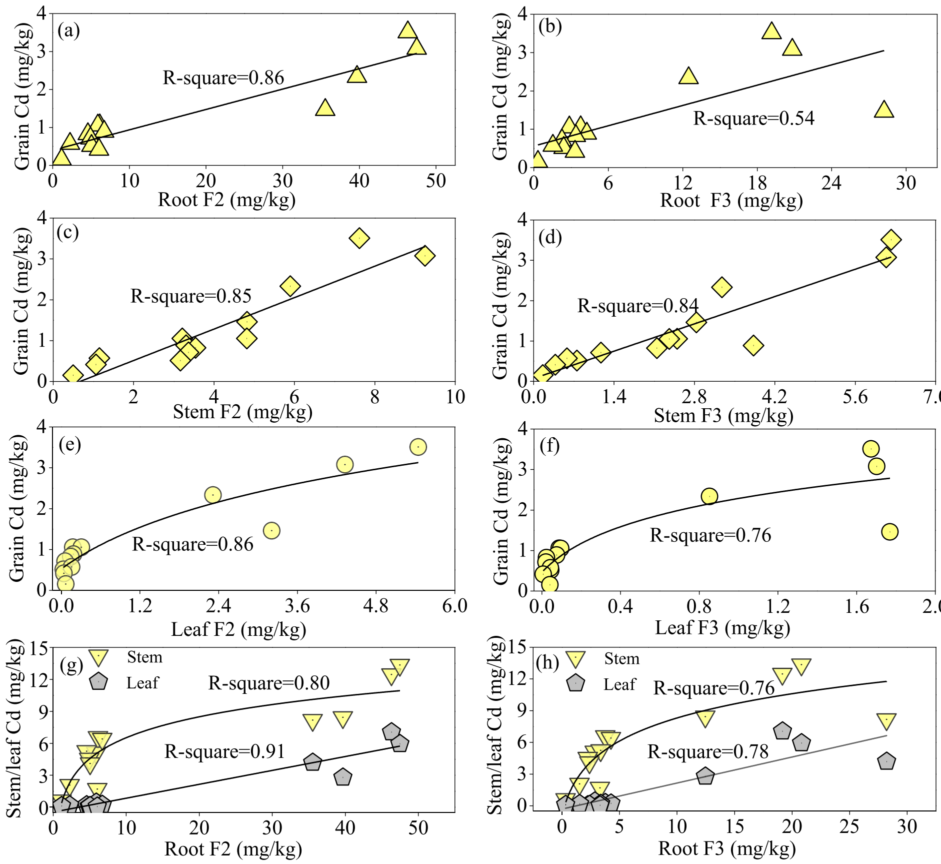

Fig. 4. Correlations between grain Cd and the Cd chemical forms (F2/F3) in the roots, stems, and leaves (a–f) and correlations between the Cd concentrations in stems/leaves and the chemical forms of Cd (F2/F3) in roots (g–h).

3.3. Health risk assessment

3.3.1. Estimated weekly intake

The values of estimated weekly intake (*EWI*) of Cd via rice consumption are shown in Fig. 5. The average value was 17×10^{-3} mg/kg BW/week, and the highest value reached 16×10^{-2} mg/kg BW/week.

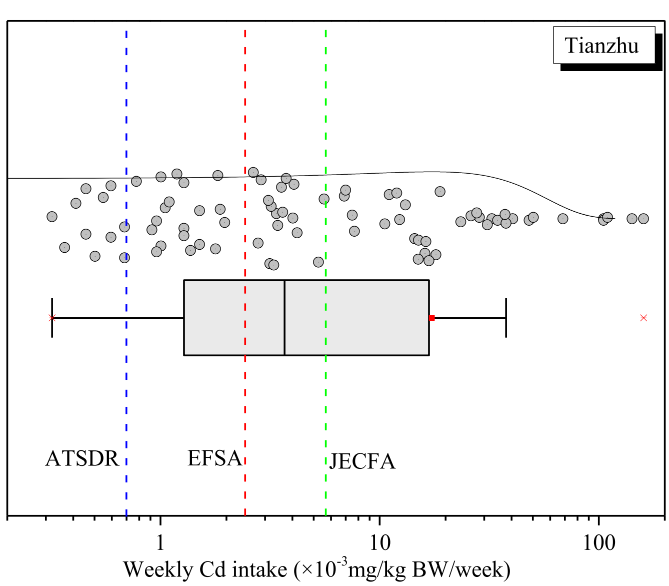

Fig. 5. Estimated weekly Cd intake for the population in the present study area via rice consumption and the provisional tolerable weekly intake for Cd established by ATSDR, EFSA and JECFA.

In China, the reported dietary intake of Cd through various foods for the national population indicated that the averages of *EWI* were 3.67×10^{-3} mg/kg BW/week and 3.57×10^{-3} mg/kg BW/week in 2014 and 2017, respectively (Yuan et al., 2014; Song et al., 2017). Compared with those values, the people living in this study area experienced higher Cd exposure levels (Fig. 5).

The joint FAO/WHO Expert Committee on Food Additives (JECFA), the European Food Safety Authority (EFSA) and the Agency for Toxic Substances and Disease Registry (ATSDR) established a provisional tolerable weekly intake (PTWI) for Cd (ATSDR (Agency for Toxic Substances and Disedse Registry), 2012; EFSA, 2009; FAO/WHO (Food and Agriculture Organization/World Health Organization), 2010). The results showed that the highest estimated weekly intake of Cd through rice consumption in this study was higher than all PTWI values recommended by those organizations (Fig. 5). Specifically, approximately 44% of our results exceeded the safe intake limit proposed by JECFA, 63% exceeded EFSA's safe intake limit, and 87% exceeded the safe intake limit recommended by ATSDR.

3.3.2. Noncarcinogenic and carcinogenic risk assessments

The *HQ* values ranged from 0.05 to 23, with an average of 2.5 (Fig. S4a). Approximately 44% of the samples in this study had *HQ* values above 1.0, indicating a high possibility of noncarcinogenic health disorders (USEPA, 2015). Compared with the value of 0.52, the reported average *HQ* value for the general adult population in China (Yuan et al., 2014), our data were 5 times higher. The *AELCR* values ranged from 0.4×10^{-5} a^{-1} to 190×10^{-5} a^{-1} (Fig. S4b), with an average of 21×10^{-5} a^{-1}. Approximately 50% of the samples exhibited *AELCR* values above 5.0×10^{-5} a^{-1}, the maximum acceptable value for carcinogens determined by the International Commission on Radiological Protection (ICRP) (Yuan et al., 2014).

Based on the probabilistic risk assessment, the $P_{95\%}$ of the *HQ* value was 13.13 (Fig. S5), far greater than 1. The noncarcinogenic adverse effect via rice consumption cannot be ignored in the study area. Similarly, the $P_{95\%}$ of the *AELCR* in the probabilistic risk assessment reached $56 \times 10^{-5}\ a^{-1}$, which was greater than the maximum acceptable value for carcinogens of Cd ($5.0 \times 10^{-5}\ a^{-1}$). Therefore, Cd exposure posed by rice consumption might cause significant carcinogenic risks for the residents. Based on the mean *AELCR* value of $4.56 \times 10^{-5}\ a^{-1}$ reported by Yuan et al. (2014) for the national population in China, the populations dwelling in the study region experienced a high cancer risk of Cd exposure.

3.3.3. Predicted urinary Cd levels

In epidemiologic research, U–Cd is used as a suitable biomarker of long-term Cd exposure (Vacchi-Suzzi et al., 2016), and this metric can reflect the Cd concentrations in human organs, particularly the liver and kidney (Satarug, 2018).

In the present study, the predicted U–Cd concentrations varied widely, from 0.25 μg/g to 125 μg/g creatinine (Fig. S6), with an average value of 13 μg/g creatinine. Ke et al. (2015a) investigated the U–Cd concentrations of 6103 participants living in Cd-polluted areas in mining and smelting areas of China and reported that the average U–Cd levels were 4.82 and 4.87 μg/g creatinine for males and females, respectively. Compared with the U–Cd threshold values set by the WHO (5.24 μg/g creatinine) and EFSA (1 μg/g creatinine) (Satarug et al., 2013), approximately 45% and 77% of the samples exceeded the values. Together, the results of the noncarcinogenic and carcinogenic risk assessments suggest that the rice Cd exposure risk in the study area is significant.

4. Conclusions

The present study first elucidated serious Cd contamination in a soil-rice system that was impacted by Ba mining. A significantly positive correlation was obtained between the soil Cd and soil Ba, suggesting that Ba mining is an important source of Cd. Concentrations as high as 91 mg/kg and 3.5 mg/kg Cd were observed in the soils and rice grains, respectively. The 0.6 M HCl-extractable fraction (F2) exhibited the largest proportion of Cd in the rice tissues, which might play a dominant role in the migration process of Cd^{2+} through rice tissues as well as in grain accumulation. The health risk assessment demonstrated that approximately 44% and 50% of the samples were higher than the safety risk levels of *HQ* (1.0) and *AELCR* ($5.0 \times 10^{-5}\ a^{-1}$), respectively, with $P_{95\%}$ values of *HQ* and *AELCR* reaching 13.13 and $56 \times 10^{-5}\ a^{-1}$, respectively. The population living in the study area has experienced a high Cd exposure risk via rice consumption. More attention should be paid to the issue of Cd contamination in Ba mining areas.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecoenv.2019.109590.

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