Hazard/Risk Assessment

Bioaccumulation and Health Risk Assessment of Heavy Metals in the Soil–Rice System in a Typical Seleniferous Area in Central China

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Abstract: Heavy metals are rich in seleniferous areas; however, the bioaccumulation and health risk of heavy metals are poorly understood, given the fact that selenium (Se) can inhibit the phytotoxicity and bioavailability of many heavy metals. The present study investigated the bioaccumulation of heavy metals in the soil–rice system in the Enshi seleniferous area of central China. Soils were contaminated by Mo, Cu, As, Sb, Zn, Cd, Tl, and Hg caused by the weathering of Se-rich shales. Among these heavy metals, Cd and Mo had the highest bioavailability in soils. The bioavailable fractions of Cd and Mo accounted for 41.84 and 10.75% of the total Cd and Mo in soils, respectively. Correspondingly, much higher bioaccumulation factors (BAFs) of Cd (0.34) and Mo (0.46) were found in rice, compared with those of other heavy metals (Zn 0.16, Cu 0.05, Hg 0.04, and Sb 0.0002). For the first time—to our knowledge—we showed that the uptake of Hg, Cd, and Cu by rice could be inhibited by the presence of Se in the soil. The probable daily intake (PDI) of Se, Cd, Mo, Zn, and Cu through consumption of local rice was 252 ± 184, 314 ± 301, and $1774 \pm 1326\,\mu g/d$; and 7.4 ± 1.68 and $0.87 \pm 0.35\,mg/d$, respectively. The high hazard quotients (HQs) of Mo (1.97 ± 1.47) and Cd (5.22 ± 5.02) suggested a high risk of Cd and Mo for Enshi residents through consumption of rice. *Environ Toxicol Chem* 2019;38:1577–1584. © 2019 SETAC

Keywords: Heavy metals; Bioaccumulation; Risk assessment; Selenium; Soil–rice system

INTRODUCTION

Heavy metals (e.g., As, Cd, Hg, and Sb) are natural constituents of the earth's crust; however, anthropogenic activities have drastically altered their geochemical cycles in the environment. In recent decades, the rapid development of China has caused heavy metal pollution and serious environmental issues (Li et al. 2014). A nationwide survey has shown that 19% of China's agricultural soils have been contaminated with heavy metals to varying degrees (Wang et al. 2014). This is of great concern because heavy metals cause adverse effects on human health and ecosystems (Fraga 2005; Zhuang et al. 2009; Fang et al. 2010; Gall et al. 2015; Toth et al. 2016; Liu et al. 2017). Heavy metals are often enriched in sulfide minerals and shales (Coveney and Glascock 1989; Derkowski and Marynowski

2018; Pearce et al. 2018). Mining and weathering of these source materials result in the release of heavy metals into the environment (Yu et al. 2011; Anjum et al. 2012), which is called multiple heavy metal pollution. This type of pollution not only degrades the quality of the soil and food crops but also threatens the well-being of food webs and human health because of the bioaccumulation of heavy metals (Fraga 2005; Zhuang et al. 2009; Fang et al. 2010; Gall et al. 2015; Toth et al. 2016; Liu et al. 2017).

A typical example of multiple heavy metal pollution can be found in Enshi, central China. As the "world's selenium (Se) capital," Enshi has the only natural, native deposit of Se in the world (Song 1989). Carbonaceous shale (also called stone coal) is the main host rock of Se in Enshi (Song 1989; Zhu et al. 2014). In the 1960s, the mining and burning of Se-rich stone coals resulted in severe Se poisoning of residents (Zhu 2004; Zhu et al. 2008). Although this Se poisoning incident occurred decades ago, inhabitants of Enshi still face the risk of excessive Se exposure as a result of the consumption of local Se-rich foods (Qin et al. 2013). It has been

reported that the long-term exploration of stone coal and the weathering of Se-rich shales in Enshi have released a substantial amount of Se into surrounding soils (Zhu et al. 2008, 2014), and that the uptake of Se from soil is the dominant pathway contributing to Se levels in rice (Williams et al. 2009; Qin et al. 2013; Chang et al. 2019). Because Se acts as an antioxidant that defends against free radical damage and inflammation, and plays a key role in maintaining a healthy metabolism, powders of Se-rich shales were recently applied into the Enshi soils for growing Se-rich agricultural products (Deng et al. 2018). In addition to the extremely high geochemical background of Se (Sun et al. 2010; Zhu et al. 2014), the enrichment of many heavy metals (e.g., Mo, Cu, Zn, Cd, As, and Sb) has also been reported in the Enshi Se-rich shales (Yao et al. 2002; Fan et al. 2008). We hypothesized that weathering, mining, and agricultural activities may result not only in the release of heavy metals from Se-rich shales but also alter the speciation and bioavailability of heavy metals, and that rice from Enshi may be contaminated because of the uptake and bioaccumulation of these heavy metals. The high organic matter and Se background in Enshi are believed to play important roles in controlling the speciation and bioavailability of heavy metals. Organic matters, which have an affinity to heavy metals, can influence the cation exchange capacity and the retention of heavy metals (Balasoiu et al. 2011). Decomposition of organic matters during weathering, mining, and agricultural activities may increase the mobility and bioavailability of heavy metals in Enshi soils. Studies have also demonstrated that Se can inhibit the uptake of heavy metals by plants (Malik et al. 2012; Zhang et al. 2012; Hu et al. 2013, 2014; Zhao et al. 2013; Wan et al. 2016; Handa et al. 2018).

The present study aimed to evaluate the environmental risk of multiple heavy metal pollution in Enshi. Local constituents (e.g., soils and rice plants) from Enshi were collected for heavy metal analysis to examine their pollution status. The bioavailable fractions of selected heavy metals (Mo, Cu, Zn, and Cd) in soils were then determined to evaluate their bioavailability. The bioaccumulation factors (BAFs) of heavy metals in rice and the human exposure risk of heavy metals through rice consumption were also explored.

MATERIALS AND METHODS

Study area and sample collection

Enshi is located in Hubei Province in central China. This area has a subtropical monsoon climate, with an annual temperature of 16 °C and annual precipitation of approximately 1600 mm (Qin et al. 2013). Both carbonaceous shale and chert strata are the major source rocks of Se in Enshi (Song 1989). The Se-rich shales have long been explored by the locals as stone coals (Zhu 2004). The weathering of Se-rich shales has resulted in the release of Se into the surrounding environment (Zhu et al. 2014). High concentrations of Se have been reported in soils, sediments, water, and plants (Zheng et al. 1992; Huang et al. 2013; Qin et al. 2013). Rice is the major economic crop and staple for the locals in Enshi.

In September 2016, arid land soils were collected from Yutangba ($n = 6$), Daping ($n = 8$), and Muli ($n = 3$), as shown in Figure 1. Paddy soils ($n = 24$) with corresponding rice plants were also collected from Muli. At each site, three 2-m × 2-m plots were established for sample collection. At each plot, 3 rice plants and corresponding rhizosphere soils (0–20-cm depth) were randomly sampled. Subsamples collected from the 3 plots were mixed as a composite sample, sealed in plastic bags, and delivered to the laboratory. Soils were then freeze-dried (–79 °C), crushed, homogenized, and sieved at a 200-mesh size. Rice tissues (root, stem, leaf, and grain) were separated, washed, dried in an oven (35 °C) until they reached a consistent weight, and powdered before further analysis. Details concerning sample preparation, determination of soil pH, concentrations of soil organic carbon, Se amounts of paddy soils, and rice tissues were reported in our recent study (Chang et al. 2019).

Heavy metal concentration analysis

Initially, 0.1 g of soil samples were digested with HNO_3 (2.5 mL) and hydrofluoric acid (HF) (0.5 mL) in an oven at 155 °C for 36 h; and 0.2 g of rice tissues were digested with concentrated HNO_3 at 155 °C for 18 h in high-pressure digestion Teflon bombs. After digestion, the bombs were unscrewed, supplemented with 2 mL of 30% (v/v) H_2O_2, and heated on a

FIGURE 1: A stretch map showing the study area and sampling sites. YTB = Yutangba; DP = Daping; ML = Muli.

hot plate (110 °C) until the solutions were evaporated to near dryness. Then 3 mL of Milli-Q water (Millipore) and 2 mL of concentrated HNO_3 were added, and the bombs were heated in an oven at 155 °C for 7 h to dissolve the residue. Heavy metals (Mo, Cd, Zn, Cu, As, Sb, and Tl) were analyzed by Nexion 300X inductively coupled plasma–mass spectrometry (PerkinElmer), according to a previously used method (Liang et al. 2000). Mercury concentrations were measured separately. Briefly, approximately 0.1 to 0.2 g of soil samples were digested in a water bath (95 °C) utilizing 5 mL of aqua regia (HCl:HNO_3 = 3:1, v/v) before measurement by F732–VJ cold vapor atomic absorption spectrometry (Agilent), adhering to an earlier reported approach (Yin et al. 2013). Approximately 0.2 g of rice samples were digested with 5 mL of HNO_3 and H_2SO_4 (4:1, v/v) and then analyzed by Tekran 2500 cold vapor atomic fluorescence spectroscopy following US Environmental Protection Agency (USEPA) Method 1631 (US Environmental Protection Agency 1999).

Certified reference materials GBW07405 (yellow–red soil), GBW10020 (citrus leaf), and sample duplicates were included during all analyses. The recoveries of all the elements were within 87 to 117% for certified reference materials. The relative variance of all measured elements was within 10% for sample duplicates.

Bioavailable fractions of heavy metals

The bioavailable fractions (water-soluble and exchangeable) of several heavy metals (e.g., Se, Mo, Cd, Cu, and Zn) were measured according to the methods summarized in Table 1. In brief, Milli-Q water was used to extract the water-soluble fractions of all the selected metals: 0.1 mol/L KH_2PO_4 was utilized to extract exchangeable Se, 0.1 mol/L NaOH was used to extract exchangeable Mo, and 1 mol/L $MgCl_2$ was used to extract exchangeable fractions of Cd, Zn, and Cu.

Health risk assessment through rice consumption

The probable daily intake (PDI) and hazard quotients (HQs) were calculated to estimate the human exposure risk of heavy metals through rice consumption for the Enshi adult population using the equations PDI = C × IR and HQ = ADD/RfD. The concentration of heavy metals in rice is represented by C; IR is the daily intake rate of rice for the adult population (425 g/d, according to Qin et al. 2013); ADD is the oral adult daily dose of heavy metals (mg/kg/d); and RfD is the oral reference dose of heavy metals (mg/kg/d). For the adult population (60 kg body wt), ADD is equal to PDI/60.

Statistical analysis

Correlation analyses were performed using IBM SPSS Ver. 22 software. Correlation coefficients (r) and significance probabilities (p) were computed for linear and nonlinear regression fits. Graphical analyses were conducted by OriginPro 2017 and Microsoft Office Ver. 365 2016 software.

RESULTS AND DISCUSSION

Heavy metal concentrations in Se-rich shales and soils

Previous studies have reported high levels of heavy metals (Se, Mo, Cd, Zn, Cu, As, Sb, and Tl) in Se-rich shales from Enshi (Yao et al. 2002; Fan et al. 2008; Zhu et al. 2014; Tian 2017). In Figure 2A, Se concentrations of these shales varied from 1.5 to 7007 µg/g, with a geometric mean of 133 µg/g that meets the ore grade level (80 µg/g). The geometric mean amounts of Mo, Cd, Zn, Cu, As, and Sb in black shales were 151.3, 4.8, 132, 78.3, 13.6, and 6.9 µg/g, respectively. These were all 1 to 3 magnitudes higher than their abundances in the earth's crust (Figure 2B). The accumulations of heavy metals were within the same range as arid land soils and paddy soils in the present study (Figure 2C). The geometric mean values of Se, Mo, Cu, As, Sb, Zn, Cd, Tl, and Hg across all the soils were 2.5, 4.6, 36.8, 11.0, 2.0, 105.5, 1.2, 0.9, and 0.12 µg/g, respectively, also 1 to 3 magnitudes higher than their abundances in the earth's crust (Figure 2D).
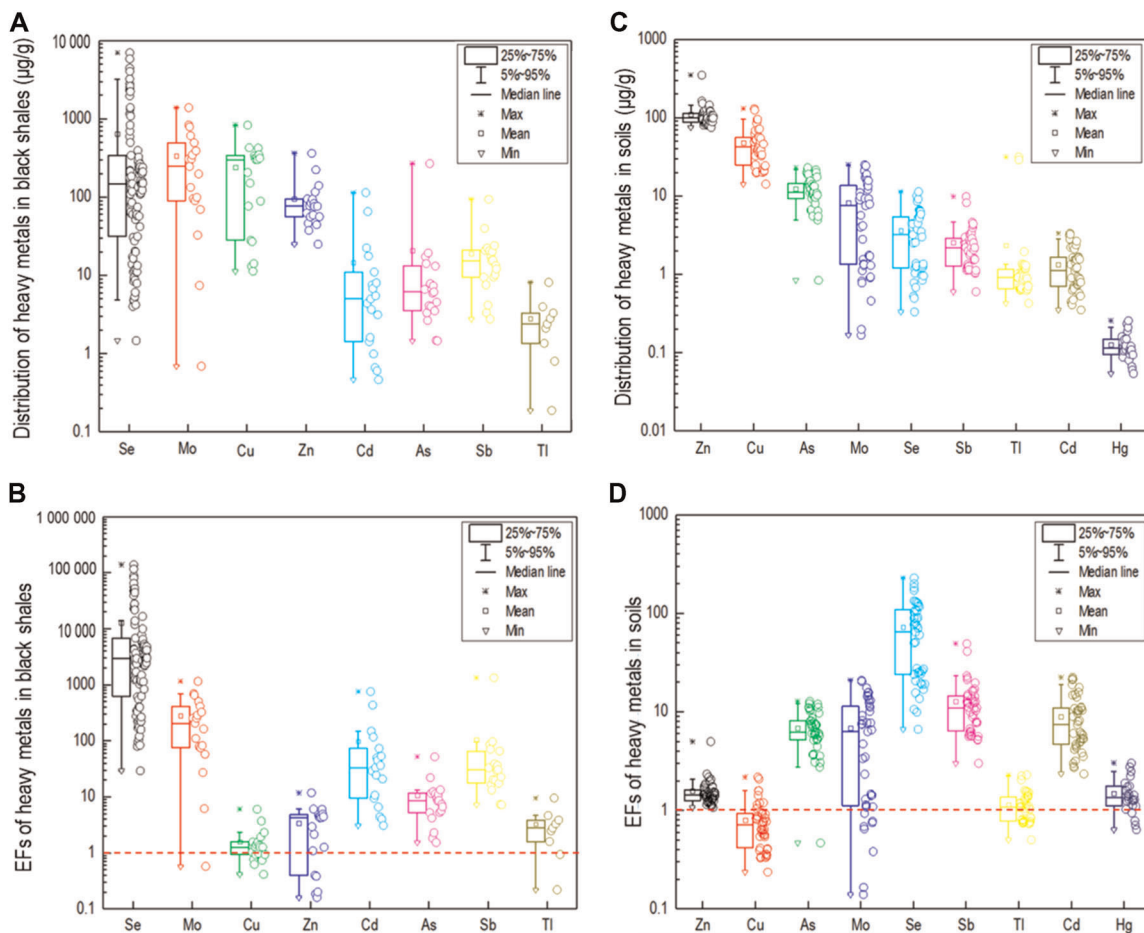
In Figure 3, the concentrations of Se, Mo, Cd, Zn, Cu, As, Sb, and Tl in shales and soils were positively correlated, suggesting that Enshi soils mainly receive these heavy metals from the weathering of Se-rich shales. Indeed, the weathering of shales provided a material basis for the formation of soils. Interestingly, the correlations of heavy metals between shales and soils were lower than the 1:1 line (especially for Se, Mo, and Cd), suggesting that these heavy metals were lost to varying degrees during the weathering of Se-rich shales. For soils, significantly positive correlations were observed between soil organic carbon and Se, Mo, Sb, Cd, Cu, Tl, and Hg (Table 2), signaling that these heavy metals were associated with soil organic matter. Such matter contains thiol groups (–SH) that may form complexes with these metals because of their chalcophile character.

Bioavailable fractions of heavy metals in soil

The bioavailable fractions (water-soluble and exchangeable) of Mo, Cd, Cu, and Zn are summarized in Table 3. For Se, Mo, and Cd, the bioavailable fractions (water-soluble and exchangeable) exceeded 10, 20, and 40% of total Se, Mo, and Cd in soils, respectively, indicating high bioavailability and high environmental risk of Se, Mo, and Cd in soils. Conversely, the bioavailable fractions of Cu and Zn accounted for only 0.5 and 1.5% of the total Cu and Zn in soils, respectively.

TABLE 1: Sequential extraction of water-soluble and exchangeable fractions of Se, Cd, Mo, Cu, and Zn in soils from Enshi, China

Elements	Fractionation	Reagent	References
Se	Water-soluble	Milli-Q water	Chang et al. 2019
	Exchangeable	0.1 M KH_2PO_4	
Mo	Water-soluble	Milli-Q water	Haley and
	Exchangeable	0.1 M NaOH	Melsted 1957
Cd, Zn,	Water-soluble	Milli-Q water	Ma and Rao 1997
and Cu	Exchangeable	1 M $MgCl_2$	

FIGURE 2: Concentrations and enrichment factors (EFs) of heavy metals in shales and soils from Enshi, China. $EF = C_{soil}/C_{crust}$, where C_{soil} refers to the amount of heavy metals in the Enshi soils, and C_{crust} denotes the abundance of heavy metals in the continental crust.

The soil samples had pH values ranging from 4.8 to 7.06, according to our recent study (Chang et al. 2019). The generation of organic acids during the decay process or oxidation of any sulfide material in the shale tended to decrease soil pH value (McCauley et al. 2009; Yun et al. 2016). Significantly

negative correlations were found between soil pH and the percentages of exchangeable Cu ($r = 0.68$; $p < 0.01$), Zn ($r = 0.68$; $p < 0.01$), and Cd ($r = 0.48$; $p < 0.05$). These reflected the weaker bonding of cationic trace metals at lower pH caused by: 1) greater proton competition for adsorption sites on
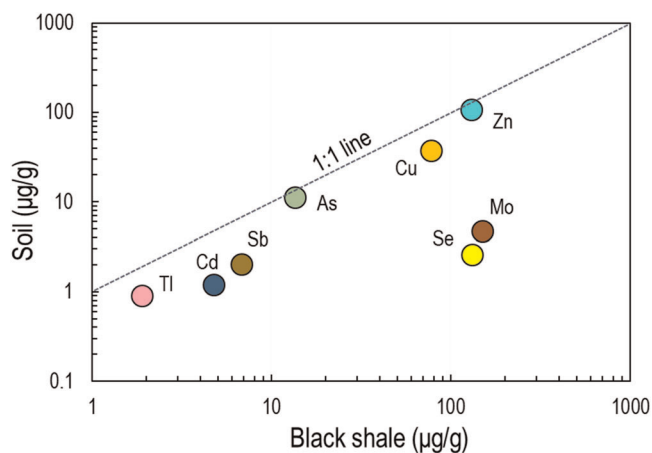
FIGURE 3: Correlations in geometric mean heavy metal concentrations between Se-rich shales and soils from Enshi, China.

TABLE 2: Pearson's correlation coefficient (r) of soil organic carbon and heavy metal concentrations in soils from Enshi, China

	Se	Mo	Cu	Sb	Hg	Tl	Cd
Soil organic carbon	0.57**	0.54**	0.33*	0.57**	0.49*	0.58**	0.37*

*Significant at $p < 0.05$.
**Significant at $p < 0.01$.

**TABLE 3:** Percentages of water-soluble and exchangeable fractions of Mo, Cd, Zn, and Cu in soils from Enshi, China

	Water-soluble (%)			Exchangeable (%)		
	Min	Mean	Max	Min	Mean	Max
Mo	0.01	0.19	1.58	6.81	10.56	18.38
Cd	0.09	0.61	1.12	27.14	41.23	58.21
Zn	0.01	0.05	0.14	0.45	1.46	3.28
Cu	0.05	0.21	0.65	0.06	0.24	0.65

humus and Fe oxides, and 2) less negative surface charge on the geocolloidal surfaces responsible for adsorption of metals. Furthermore, positive correlations were found between both water-soluble Zn and Cd ($r = 0.49$; $p < 0.05$) and between both water-soluble Se and Mo ($r = 0.87$; $p < 0.01$) that showed that Zn and Cd and Se and Mo migrate together under similar hydrodynamic conditions. Moreover, exchangeable Cu was positively linked with exchangeable Zn ($r = 0.82$; $p < 0.01$); however, no connections were observed between exchangeable Zn and Cd ($p > 0.05$).

Bioaccumulation of heavy metals in rice

The distributions of heavy metal concentrations and BAFs in polished rice are shown in Figure 4. The geometric mean concentrations of Zn, Mo, Cu, Se, Cd, As, Hg, Tl, and Sb in rice were 17.0, 3.2, 1.9, 0.46, 0.4, and 0.12 µg/g; and 5.2, 0.44, and 0.31 ng/g, respectively. In particular, Cd in rice significantly exceeded the maximum allowable amount of Cd in food (0.2 mg/kg) set by China (National Health and Family Planning Commission of the People's Republic of China and China Food and Drug Administration 2017). The geometric mean BAFs of heavy metals in rice decreased in the following order: Mo (0.46) > Cd (0.34) > Zn (0.16) > Se (0.13) > Cu (0.05) > Hg (0.04) > As (0.01) > Tl (0.0005) > Sb (0.0002). The very high BAFs of Cd and Mo (Figure 4B) suggest that they, as opposed to the other metals, are more readily accumulated by rice. This result is consistent with their high bioavailability in the soil. See *Bioavailable fractions of heavy metals in soil* in the *Results and Discussion* section for more information.

The concentrations of Zn, Mo, and Se in rice (Figure 5) were positively correlated with their bioavailable fractions in soil; nevertheless, this was not the case for Hg, Cd, and Cu. The lack of these relationships for Hg, Cd, and Cu may be caused by the high Se levels in the Enshi soils. Studies have revealed that Se can inhibit the uptake of heavy metals by plants (Malik et al. 2012; Zhang et al. 2012; Hu et al. 2013, 2014; Zhao et al. 2013; Wan et al. 2016; Handa et al. 2018). The BAFs of Hg in rice (Figure 6A) decreased with increasing soil Se accumulation, which is consistent with a previous study in the Wanshan mercury mine in China (Zhang et al. 2012). The formation of insoluble Se-Hg compounds in soils may be the mechanism for the inhibition of Hg uptake and bioaccumulation in plants (McNear et al. 2012; Zhang et al. 2012; Zhao et al. 2013; Li et al. 2015; Tang et al. 2016). In the present study, we observed for the first time that the elevated soil Se levels in Enshi may inhibit the uptake and bioaccumulation of Cu and Cd by rice. The molar ratios of Se to Cd and Se to Cu for the Enshi soils were 5.4 ± 3.2 and 0.10 ± 0.05, respectively, much higher than those of the continental crust (Se to Cd = 0.65; Se to Cu = 0.0008). The BAFs of Cu and Cd in rice (Figure 6B,C) were also negatively correlated with soil Se concentrations ($p < 0.01$). The formation of Cu selenides, which would largely decrease the bioavailability of Cu, has been observed in Enshi soils (Zhu et al. 2012). Recent research has also shown that the addition of Se to soils can significantly reduce Cd translocation and
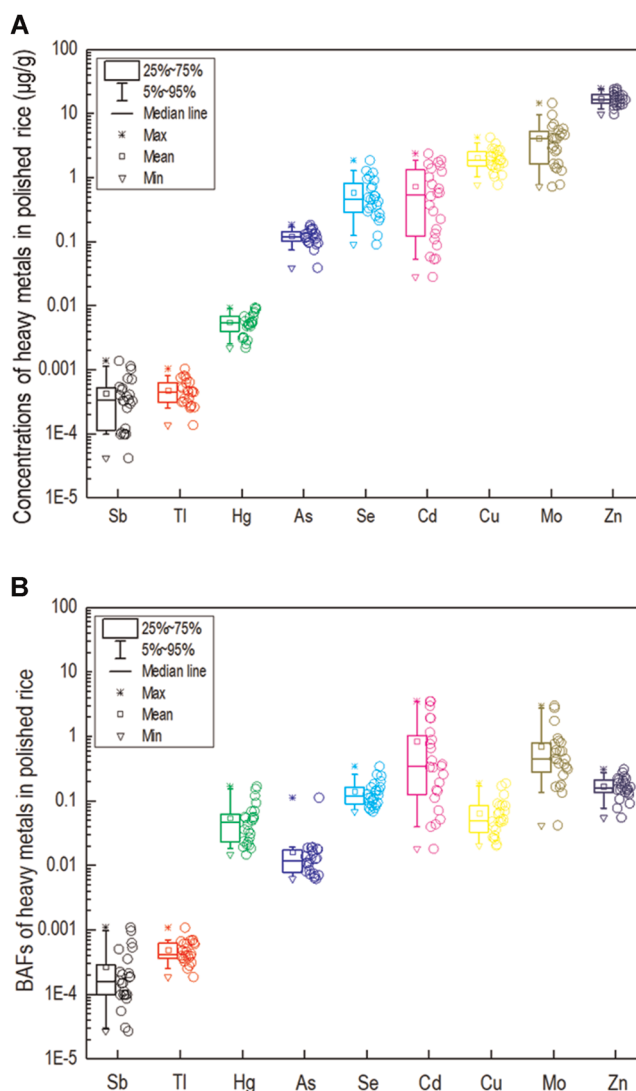
FIGURE 4: (**A**) Concentrations and (**B**) BAFs of heavy metals in rice from Enshi, China. BAFs = bioaccumulation factors.

bioaccumulation in rice (Lin et al. 2012; Hu et al. 2014; Zhao et al. 2019), which supports our results in the present study. Unlike the BAFs of Hg, Cd, and Cu, those of other heavy metals showed no clear correlations with soil Se concentrations, suggesting that soil Se has a limited impact on the bioavailability of these heavy metals.
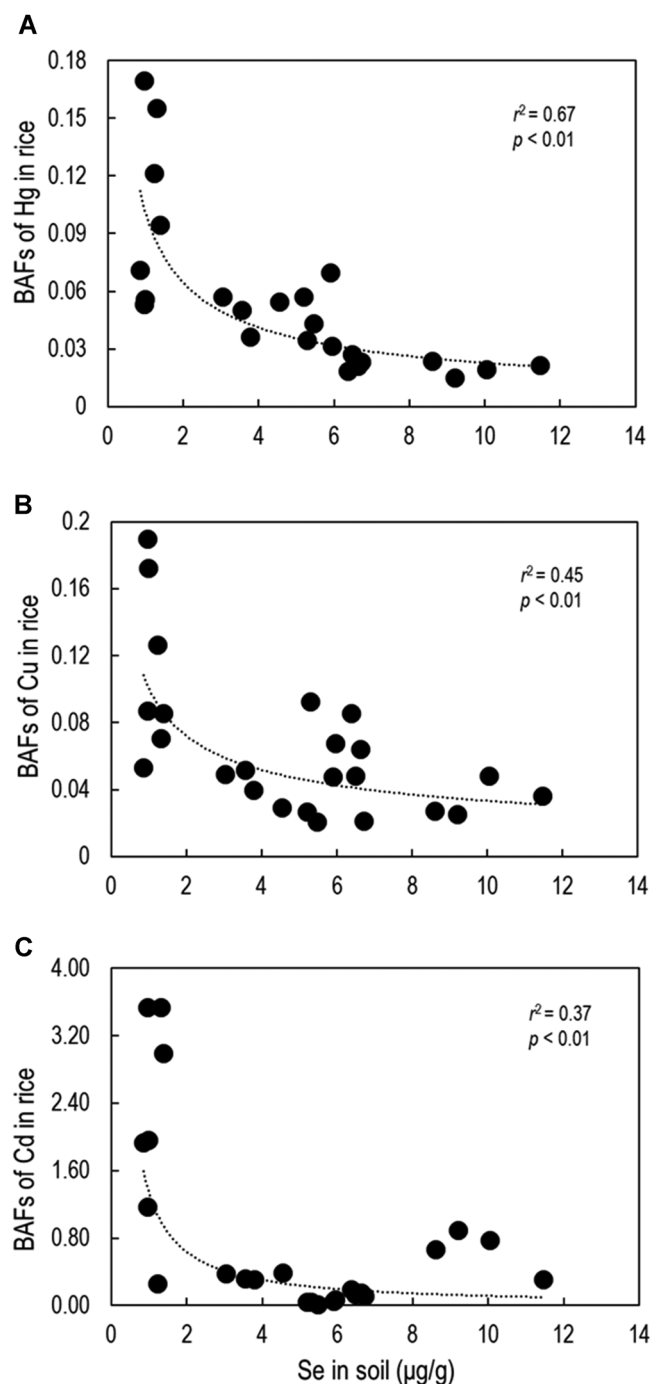
Risk assessment for heavy metals in Enshi rice

The PDI values of Se, Zn, Mo, Cu, Cd, As, Hg, Tl, and Sb are given in Figure 7. The average PDI of Se was 252 ± 184 µg/d, which exceeded the recommended nutrient intake (RNI; 60 µg/d) but was lower than the tolerable upper intake level (TUIL; 400 µg/d) set by the China Nutrition Association (Cheng 2014). The standard PDIs of Zn and Cu were 7.4 and 0.87 mg/d, respectively, which were equivalent to their RNI values (Zn 7.5 mg/d; Cu 0.8 mg/d) but much lower than their TUIL values (Zn 40 mg/d; Cu 8 mg/d). The typical PDI of Mo
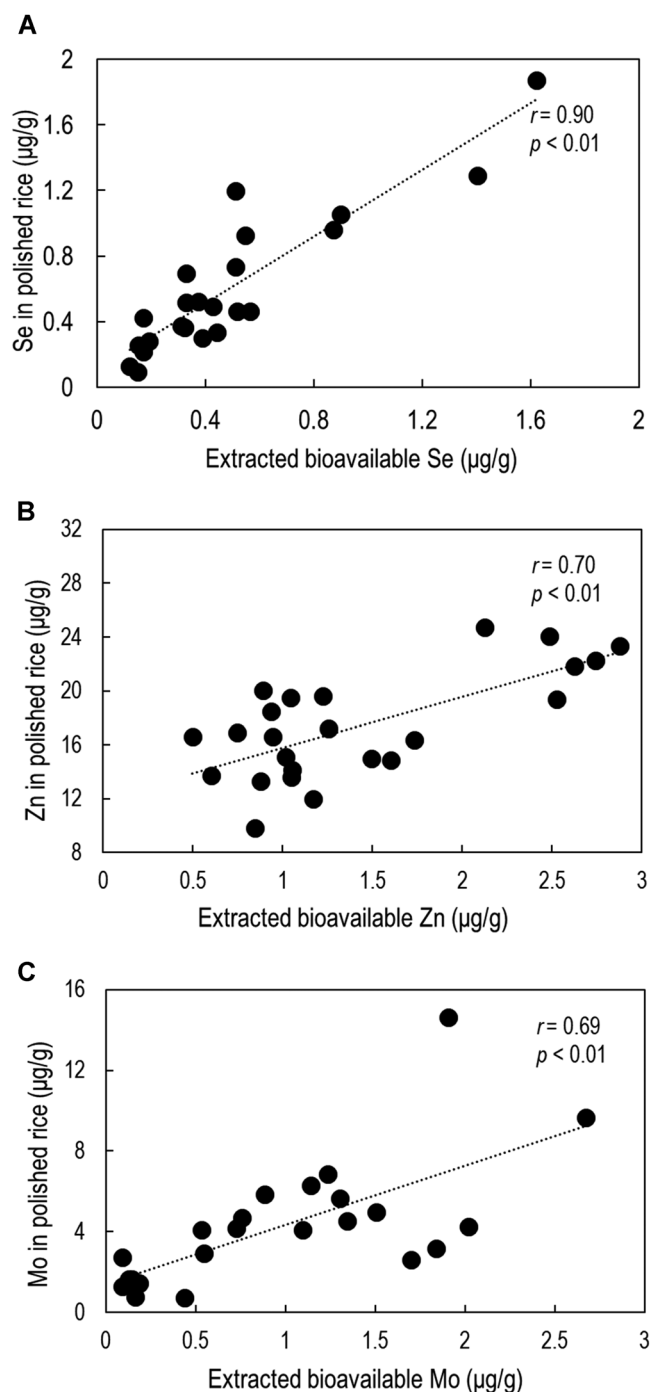
FIGURE 5: (A) Correlation between soil bioavailable Se and rice Se concentrations. (B) Relationship between soil bioavailable Zn and rice Zn amounts. (C) Link between soil bioavailable Mo and rice Mo collections.


FIGURE 6: (A) Correlations between soil Se concentrations and bioaccumulation factors (BAFs) of Cu in rice. (B) Links between soil Se collections and BAFs of Hg in rice. (C) Relationships between soil Se accumulations and BAFs of Cd in rice.

$(1774 \pm 1326\,\mu g/d)$ was much higher than the TUIL value $(900\,\mu g/d)$ established by the China Nutrition Association (Cheng 2014). The HQ of Mo ranged from 0.34 to 6.92, with a usual value of 1.97 ± 1.47; thus the excessive intake of Mo may cause negative effects on human health (Goldhaber 2003).

The average PDI levels of Cd, As, Hg, Tl, and Sb were 314 ± 301, 52.4 ± 13.8, 2.4 ± 0.9, 0.2 ± 0.1, and $0.18 \pm 0.15\,\mu g/d$ (Figure 7). The PDIs of As and Hg were lower than the

provisional permissible tolerable weekly intake values (As 128. $6\,\mu g/d$; Hg $13.5\,\mu g/d$; converted to 60 kg wt) obtained from the United Nation's Joint Food and Agriculture Organization of the United Nations/World Health Organization Expert Committee on Food Additives (Fang et al. 2010; Bolan et al. 2017). However, the PDI of As exceeded the chronic oral reference dose values ($18\,\mu g/d$; converted to 60 kg wt) obtained from the Integrated Risk Information System of USEPA (Fang et al. 2010).
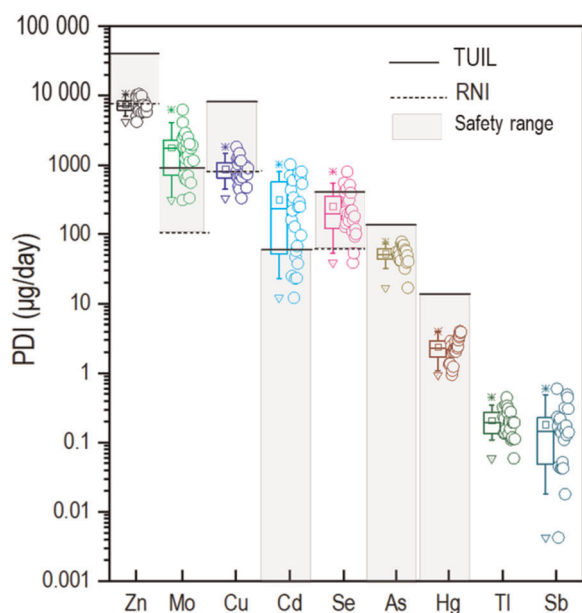
FIGURE 7: Probable daily intake (PDI) levels of heavy metals for rice consumption in Enshi, China. TUIL = tolerable upper intake level; RNI = recommended nutrient intake.

The PDI of Cd is 5 times higher than its permissible tolerable weekly intake value (60 µg/d; converted to 60 kg wt), and the HQ of Cd is approximately 5 (0.0052/0.001 mg/kg/d), which all suggest a high risk of Cd exposure as a result of rice consumption. Indeed, extremely high Cd levels were observed in the hair (17.0 ± 5.8 µg/g) and blood (7.9 ± 0.8 µg/g) of local residents from Enshi (Zhou et al. 1991).

CONCLUSIONS

In Enshi, the enrichment of heavy metals (Mo, Cd, Zn, Cu, As, Sb, Tl) has been previously reported in Se-rich shales (Yao et al. 2002; Fan et al. 2008; Zhu et al. 2014; Tian 2017). In the present study, we determined that the weathering of Se-rich shales has resulted in the intensive release of heavy metals into soils, thus causing so-called multiple heavy metal pollution in Enshi soils. Among these heavy metals, Cd and Mo have an extremely high bioavailability in the soil that corresponds to the high BAFs of Cd and Mo in rice. Enshi rice is contaminated by Cd and Mo. Risk assessment further indicated that in Enshi— even at Se concentrations that produce a Se intake rate that is more than 4 times the recommended value (252 vs 60 µg/d)— the HQ of Cd is approximately 5. Thus the Se content of the shale parent material provides only very limited protection against Cd toxicity.

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