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RESEARCH ARTICLE

Accumulation, translocation, and assessment of heavy metals in the soil-rice systems near a mine-impacted region

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Abstract

Paddy rice is considered as a main source for human exposure to heavy metal contamination due to its efficient accumulation of heavy metals especially when cultivated in contaminated fields. In the current study, rice grains, straws, roots, and rhizosphere paddy soils were collected from Changsha, a non-ferrous mine-impacted area in China. Heavy metals including Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba, and Pb in the samples were determined using ICP-MS. The heavy metal concentrations were found in the ascending order of grain < straw < root < paddy soil except As and Cd. Rice root is a main organ to retain As and Cd through chelation and adsorption. The translocation behaviors of the heavy metals in the soil-rice system were investigated through bioaccumulation factor (BF) and translocation factor (TF). Similar variation tendencies to decrease $BF_{p\text{-}r}$ (translocation from paddy soil to root) and $TF_{s\text{-}g}$ (translocation from straw to grain) associated with $TF_{r\text{-}s}$ (translocation from root to straw) increasing were observed for most of the heavy metals due to heavy metal detoxification and stress tolerance in rice. The potential adverse effects caused by long-term exposure to heavy metals from rice consumption were evaluated via the target hazard quotient. The results indicated potential health risk to human from exposure to Mn, As, and Cd.

Keywords Paddy rice · Correlation analysis · Bioaccumulation factor · Translocation factor · Target hazard quotient

Introduction

Heavy metal contamination has become a worldwide concern on account of the characteristics of persistence and biotoxicity (Chen et al. 2018, Jia et al. 2017). The heavy metal contamination in environment is mainly derived from natural origination and anthropogenic activities, of which the latter one made predominant contribution on most contaminated fields. In China, the environment has been heavily polluted by various hazardous materials including heavy metals with rapid industrialization and urbanization in recent decades (Zhao et al. 2015, Zhao et al. 2010). According to the surveys, over 10% of agricultural soils in China were contaminated to different degrees by heavy metals due to human activities such as herbicide/pesticide usage, waste water irrigation, fuel combustion, solid waste disposal, and mining and smelting processes (Zhao et al. 2015). Heavy metal contents in agricultural soils may not only reduce crop production inevitably; this contamination could be transmitted from agricultural soils to the crops then to human beings through the food consumption, posing considerable potential health risks.

There are several routes such as inhalation of dust, direct ingestion of soils, and consumption of food crops for transmission of heavy metal contamination from soils to human beings. Among them, food consumption was recognized as the main route for heavy metal transmission (Zheng et al. 2007). The biotoxicity of heavy metal contamination is dependent not only on the concentrations but also on the exposure duration through continuous consumption of contaminated food. Long-term exposure to low level of toxic elements from food consumption could still induce damage in organs or human health (Robson et al. 2014). For example, low-level exposure to lead (Pb) can significantly elevate blood lead level, which is considered as causative factors in numerous

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neurological diseases and renal impairment (Patrick 2006). Exposure to cadmium (Cd) may lead to its accumulation in the liver and kidney, which is correlated to diabetes and diabetes-related kidney diseases (Robards and Worsfold 1991). Long-term exposure to arsenic (As) may induce to skin cancer and several other effects on cardiovascular and hematopoietic system (Mandal and Suzuki 2002).

Paddy rice (*Oryza sativa* L.) and its production are the staple food for almost half of the people in the world (Stone 2008). Once uptake from paddy soils, heavy metal contamination can be transferred from rice roots to stems and leaves, and finally to rice grains. Different from other terrestrial crops, paddy rice is efficient to accumulate heavy metal contamination in both edible and inedible parts due to its cultivation in flooded paddy soil with more bioavailable heavy metals than drained soil (Carey et al. 2010, Norton et al. 2014, Wang et al. 2016). Rice consumption was considered as an important pathway of human exposure to heavy metal contamination (Islam et al. 2014, Praveena and Omar 2017). The rice grains grown in mine-impacted fields were observed to contain high levels of Pb, Cd, and As (up to 2749, 1456, and 624 μg/kg, respectively) (Norton et al. 2014, Wang et al. 2018, Zhu et al. 2008), considerably greater than the regulated threshold values in China (China Food Standard Agency 2017). Since the residual parts of rice plant such as straws (stems and leaves) are commonly treated as a livestock feed (Fu et al. 2008), heavy metals accumulated in rice straw and root could still be transferred to human through food chain. Therefore, it is necessary to profile the distribution pattern and accumulation characteristic of heavy metals in rice plant tissues and the corresponding rhizosphere soils.

Hunan Province is located in the central south part of China. Due to its abundant mineral deposits and developed mine processing industries, this province is known as a nonferrous center. Moreover, Hunan Province produced over 9.5% of total rice output in China. As a result of long-term mining and smelting activities, the surrounding agriculture soils in Hunan Province were reported to be remarkably contaminated by heavy metal pollutions (Wei et al. 2009). Higher levels of heavy metals in paddy fields normally led to more accumulation of heavy metals in rice plants (Li et al. 2012). Investigating bioaccumulation ability and translocation behavior of various heavy metals in the soil-rice system would be helpful for further remediation of heavy metal contamination. As the capital of Hunan Province, Changsha City has been impacted by heavy metal pollutions from mining and smelting activities (Jia et al. 2018b, Ma et al. 2016b). The aims of this study were (1) to evaluate the heavy metal pollution levels in paddy soils, rice roots, straws, and grains collected from a mine-impacted region near Changsha City; (2) to investigate the distribution characteristics and translocation behaviors of heavy metals in the soil-rice system; and (3) to assess potential health risk from exposure to heavy metal contamination through rice consumption.

Methods and materials

Sample collection and preparation

Changsha City (111° 54′–114° 15′ E, 27° 51′–28° 40′ N) is the capital of Hunan Province. The permanent resident population of this city is approximately 7.91 million. There are various mineral resources including manganese, copper, lead, zinc, and phosphorus in Changsha. Ten large-sized and sixteen small-sized mineral deposits are located within this region. Mining and smelting activities were initiated early in the nineteenth century and have been developed rapidly since the 1950s. As the economic center in Hunan Province, Changsha is a rapid developing city where non-ferrous mining and metallurgy are the economic mainstays. The soils around Changsha have been polluted by heavy metal contamination during the recent decades due to long-term mining and smelting activities (Ma et al. 2016b, Wang et al. 2010). The sampling fields are located in southern part of Changsha City (112.91° E, 28.02° N). A total of 27 paddy fields (ca. 1000 m^2 for each field) were selected as sampling fields. At each field, samples were collected from three subpoints and combined as one representative sample. After sent to the laboratory, rice grains, straws, roots, and corresponding paddy soils were separated. The rice grains, straws, and roots were washed with tap water to remove dust. Then the rice plant samples were rinsed using deionized water (18.2 MΩ·cm) for several times. The samples were dried in an oven at 50 °C for 48 h, and then the grains were dehusked. Afterwards, the husked grains, straws, and roots were ground and passed through a 0.2-mm nylon sieve severally to obtain homogeneous powders. The paddy soils were air dried, ground, and passed through a 0.15-mm nylon sieve. Before digestion, all the homogenous samples were kept in sealing polyethylene bags which were stored in desiccators.

Heavy metal analysis

The rice plant tissue samples were digested using the microwave assisted method described in our previous study (Ma et al. 2016a). Briefly, 0.5 g of the tissue sample was weighed into a polytetrafluoroethylene vessel in addition with 8 mL of concentrated HNO_3 (70%) and 2 mL of H_2O_2 (30%) and was digested according to the following program: 15 min to 120 °C, 15 min to 190 °C, and 30 min at 190 °C. USEPA Method 3051A (USEPA 2007) was employed for microwave-assisted digestion of soil samples with minor modification. In brief, 0.1 g of the soil sample mixed with 9 mL of HNO_3 and 3 ml of HCl was digested according to the program as follows: 15 min to 120 °C, 15 min to 210 °C, and 30 min at 210 °C.

The digested solution was cooled down to room temperature, passed through a 0.22-μm membrane filter, and then diluted in a 50-mL volumetric flask with deionized water. The diluted solution was kept at 4 °C until elemental analysis. For each batch of sample pretreatment, a method blank was performed to be free from the interferences of sample processing. The concentrations of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba, and Pb were determined by ICP-MS (Agilent 7700×). The detailed operating information on ICP-MS was listed in Table S1. The interference from polyatomic ions (e.g., $^{40}Ar^{12}C^{+}$, $^{35}Cl^{16}O^{1}H^{+}$ on m/z 52, and $^{40}Ar^{35}Cl^{+}$ on m/z 75) was eliminated by a collision cell using He as the collision gas (Sun et al. 2015). The precision and accuracy of the elemental analysis were verified by the standard reference materials GBW 07443 (paddy soil), GBW 10049 (green onion), and GBW 10045 (rice flour), which were obtained from CRM/RM information center (Beijing, China). The recoveries ($n = 5$) for the investigated heavy metals ranged from 83 to 112%.

Bioaccumulation factor and translocation factor

The translocation behaviors of the heavy metals in the soil-rice system were investigated through bioaccumulation factor (BF) and translocation factor (TF) (Ma et al. 2017a). The factors were defined based on the equations as follows:

$$BF_{i,\ p-r} = C_{i,\text{root}}/C_{i,\text{soil}} \tag{1}$$

$$TF_{i,r-s} = C_{i,\text{straw}}/C_{i,\text{root}} \tag{2}$$

$$TF_{i,s-g} = C_{i,\text{grain}}/C_{i,\text{straw}} \tag{3}$$

where $C_{i,\ \text{grain}}$, $C_{i,\ \text{straw}}$, $C_{i,\ \text{root}}$, and $C_{i,\ \text{soil}}$ are the concentrations of heavy metal i in grain, straw, root, and paddy soil, respectively. $BF_{i,\ p-r}$ is the accumulation factor of heavy metal i from paddy soil to root. $TF_{i,\ r-s}$ and $TF_{i,\ s-g}$ are the translocation factors of heavy metal i from root to straw and from straw to grain, respectively.

Risk assessment

The potential health risk to the consumers from chronic exposure to individual heavy metal through rice consumption was evaluated by the target hazard quotient (THQ) (USEPA 1989). The calculation of THQ was proposed by USEPA as the following equation:

$$EDI_i = \frac{C_i \times DI}{BW} \tag{4}$$

$$THQ_i = \frac{EDI_i}{RfD_i} \times \frac{EF \times ED}{AT} \tag{5}$$

where EDI_i (mg/BWkg·day) is the estimated daily ingestion of heavy metal i, C_i (mg/kg) is the concentration of heavy metal i in the rice grains, DI (kg/day) is the daily ingestion rate of rice, BW (BWkg) is the body weight of local inhabitants in Hunan Province, China, THQ_i is the target hazard quotient of heavy metal i, and RfD_i (mg/BWkg·day) is the oral reference dose for heavy metal i regulated by USEPA. In Eq. (5), EF (365 days/year) is the exposure frequency, ED (70 years) is the exposure duration, and AT (25,550 days) is the average exposure time (Jia et al. 2018a).

The overall health risk related to all the heavy metals was estimated by the hazard index (HI) as follows:

$$HI = \sum_{i=1}^{n} THQ_i \tag{6}$$

In the current study, the average DI and BW for local adult inhabitants in Hunan Province were 0.425 mg/kg and 58.1 BWkg, respectively (Wang et al. 2018). The RfD values for Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba, and Pb were 1.5, 1.4×10^{-1}, 7.0×10^{-1}, 3.0×10^{-4}, 1.1×10^{-2}, 4.0×10^{-2}, 3.0×10^{-1}, 3.0×10^{-4}, 1.0×10^{-3}, 2.0×10^{-1}, and 4.0×10^{-3} mg/BWkg·day, respectively (USEPA 2015).

Statistical analysis

The relationships between concentrations of individual heavy metal in rice plant tissues and corresponding paddy soil were evaluated by Pearson's correlation analysis. The significant differences at the 0.05 level among concentrations of individual heavy metal in rice plant tissues and soil were determined by one-way analysis of variance (ANOVA). Pearson's correlation analysis and ANOVA were conducted using SPSS v.13.0 for windows.

Results and discussion

Heavy metal concentrations in paddy soils and rice plant tissues

The descriptive statistical values of heavy metal concentrations including mean, standard deviation (SD), minimum, maximum, and coefficient of variation (CV) in rice plant tissues and corresponding paddy soils collected from the mine-impacted region are summarized in Table 1. The distribution patterns for most heavy metals in the soil-rice system were in the ascending order of grain < straw < root < paddy soil with significant difference ($p < 0.05$). As listed in Table 1, the paddy soils contained the highest average concentrations of Cr, Fe, Co, Ni, Cu, Zn, Ba, and Pb. However, there were some exceptions to the accumulation behavior, e.g., the rice roots accumulated more concentrations of As and Cd than other tissues and soils. This is due to the retention and adsorption of As and Cd in rice roots (Nocito et al. 2011).

Table 1 Descriptive data of heavy metal concentrations in soils, roots, straws, and grains

Heavy metal		Concentration (mg/kg)				Threshold value [a] (grain)	Background value [b] (soil)	Threshold value [c] (soil)
		Grain	Straw	Root	Paddy soil			
Cr	Mean ± SD	0.444 ± 0.502^{A}	18.1 ± 6.2^{B}	14.8 ± 7.5^{B}	53.6 ± 10.5^{C}	1.0	71.4	90
	(min-max)	(0.016–2.06)	(5.47–26.4)	(6.94–40.2)	(28.8–77.4)			
	CV	114%	41%	51%	20%			
Mn	Mean ± SD (min-max)	31.3 ± 7.1^{A}	697 ± 284^{B}	341 ± 186^{C}	367 ± 178^{C}	–	459	–
	CV	(22.1–46.2)	(228–1670)	(111–887)	(140–782)			
		23%	41%	54%	49%			
Fe	Mean ± SD	20.2 ± 9.4^{A}	178 ± 31^{B}	25,600 ± 11000^{C}	26,000 ± 3500^{C}	–	39,600	–
	(min-max)	(10.2–53.8)	(92.8–235)	(8910–55,400)	(17600–33,000)			
	CV	47%	18%	43%	13%			
Co	Mean ± SD	0.019 ± 0.006^{A}	0.333 ± 0.114^{B}	3.70 ± 1.07^{C}	11.0 ± 1.9^{D}	–	14.6	–
	(min-max)	(0.010–0.031)	(0.075–0.558)	(1.85–6.37)	(8.38–15.8)			
	CV	29%	34%	29%	17%			
Ni	Mean ± SD	0.343 ± 0.258^{A}	6.86 ± 3.11^{B}	5.27 ± 2.45^{B}	23.3 ± 2.4^{C}	–	31.9	40
	(min-max)	(0.057–1.07)	(1.20–10.5)	(2.16–13.4)	(17.4–28.6)			
	CV	75%	51%	47%	10%			
Cu	Mean ± SD	3.69 ± 1.70^{A}	3.27 ± 1.93^{A}	11.2 ± 5.7^{B}	23.9 ± 5.9^{C}	10	27.8	35
	(min-max)	(0.956–7.28)	(0.966–7.30)	(4.06–25.5)	(15.0–43.7)			
	CV	53%	59%	51%	25%			
Zn	Mean ± SD	17.7 ± 2.6^{A}	31.1 ± 9.6^{B}	39.7 ± 10.2^{C}	82.7 ± 23.7^{D}	50	94.4	100
	(min-max)	(12.7–23.7)	(17.0–50.2)	(20.8–54.9)	(49.8–143)			
	CV	15%	31%	26%	29%			
As	Mean ± SD	0.204 ± 0.072^{A}	2.50 ± 1.71^{B}	110 ± 87^{C}	15.1 ± 4.1^{D}	0.2[d]	15.7	15
	(min-max)	(0.059–0.339)	(0.404–5.85)	(19.6–383)	(9.14–25.9)			
	CV	35%	68%	79%	27%			
Cd	Mean ± SD	0.291 ± 0.295^{A}	0.802 ± 0.839^{AB}	3.53 ± 2.60^{C}	0.732 ± 0.362^{B}	0.2	0.126	0.2
	(min-max)	(0.011–1.07)	(0.026–3.11)	(0.232–9.70)	(0.290–1.60)			
	CV	131%	126%	105%	49%			
Ba	Mean ± SD	1.52 ± 0.85^{A}	94.4 ± 34.5^{B}	80.9 ± 42.8^{B}	279 ± 98^{C}	–	383	–
	(min-max)	(0.453–3.49)	(34.6–168)	(37.4–198)	(162–595)			
	CV	56%	37%	53%	35%			
Pb	Mean ± SD	0.031 ± 0.023^{A}	1.07 ± 0.61^{B}	27.8 ± 22.3^{C}	51.2 ± 15.0^{D}	0.2	29.7	35
	(min-max)	(0.003–0.088)	(0.479–3.12)	(10.2–109)	(31.3–90.6)			
	CV	170%	57%	80%	29%			

Different capital letters in the same row indicate significant differences at $p < 0.05$

[a] Chinese maximum contaminant levels for rice regulated by China Food Standard Agency

[b] Soil background values for heavy metals in Hunan Province of China

[c] Environmental quality standard for soils in China, grade I

[d] Regulated for inorganic As

In order to evaluate heavy metal pollutions in the paddy soils, the background element concentrations in the soils from Hunan Province, China (China National Environmental Monitoring Centre 1990) and the environmental quality standard values for soils in China (grade I) (China National Environmental Monitoring Centre 1995) were employed as shown in Table 1. The average concentrations of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, and Ba in the paddy soils were below or comparable to the background values, indicating there was no anthropogenic pollution related to these heavy metals. On the contrary, the minimum values of Cd and Pb in the paddy soils were 0.290 and 31.3 mg/kg, respectively, both exceeding the background values. Moreover, the average concentrations of Cd and Pb were 0.731 and 51.2 mg/kg, respectively, 3.66 and 1.46 times higher than the threshold values. Relatively, high contents of Cd and Pb were also observed in other adjacent parts of Hunan Province, especially in the middle and lower Xiang River, the main river in Hunan Province (Wang et al. 2008). This phenomenon can be attributed to long-term mining and smelting processes of lead-zinc deposits in the upstream area (Wei et al. 2009).

The threshold values of Cr, Cu, Zn, inorganic As, Cd, and Pb regulated by China Food Standard Agency (China Food Standard Agency 2017) were employed to evaluate the heavy metal contamination in rice grains. As presented in Table 1, the average concentrations of Cr, Cu, Zn, As, Cd, and Pb in the rice grains were 0.444, 3.69, 17.7, 0.204, 0.291, and 0.031 mg/kg, respectively, lower than the threshold values except As and Cd. In the analyzed rice grain samples, 56% of As and 44% of Cd exceeded the regulated threshold values in rice. The average proportion of inorganic As in rice grains collected no matter from Hunan Province or other regions in China were over 90% in the published reports (Ma et al. 2017a, Ma et al. 2017b). Assuming the toxic inorganic As to be 90% of total As, there were still half of the collected rice grain samples exceeding the threshold value for inorganic As. The accumulations of As and Cd have been widely investigated in recent years. The results showed efficient transfer of both As and Cd from rice root to rice grain (Lu et al. 2009, Wang et al. 2016). Furthermore, the rice grains with high As content could be produced even in low soil As paddies (Lu et al. 2009).

Correlations of heavy metal concentrations

The relationships between the concentrations in paddy soil and root, root and straw, and straw and grain for individual heavy metal are illustrated in Fig. 1. No significant relationship at 0.01 or 0.05 level was found for Cr, Fe, and Ni, indicating that the concentrations of these elements in rice grains were irrelevant to those in paddy soils or other parts of rice plants. Lack of correlation for Fe is due to the formation of iron plaques on the root surface, which also restrict uptake of

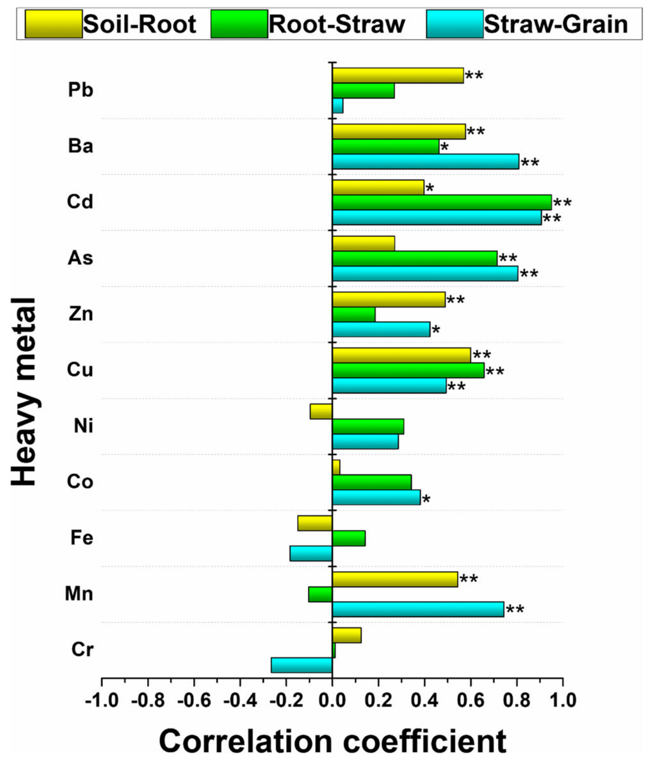

Fig. 1 Correlations between individual heavy metal concentrations in soils, roots, straws, and grains

Ni by rice roots (Ye et al. 1997). There are two Cr species, Cr(VI) and Cr(III), present in the soils. Cr(III) with lower toxicity and mobility is the main form in the reductive condition of the flooded soil (Liu et al. 2007). Therefore, the bioavailability of Cr was low in the paddy soil due to poor solubility and low mobility of Cr(III). Significant positive correlations between the concentrations in paddy soil and root were observed for Mn ($r = 0.543$, $p < 0.01$), Cu ($r = 0.600$, $p < 0.01$), Zn ($r = 0.489$, $p < 0.01$), Cd ($r = 0.397$, $p < 0.05$), Ba ($r = 0.577$, $p < 0.01$), and Pb ($r = 0.569$, $p < 0.01$). However, significant relationships between the concentrations in root and straw were only found for Cu ($r = 0.658$, $p < 0.01$), As ($r = 0.715$, $p < 0.01$), Cd ($r = 0.950$, $p < 0.01$), and Ba ($r = 0.462$, $p < 0.05$). This is due to the restriction of heavy metals in rice roots from transferring to the aerial parts (Zhou et al. 2015). Between the concentrations in straw and grain, significant correlations were found for Mn ($r = 0.744$, $p < 0.01$), Co ($r = 0.382$, $p < 0.05$), Cu ($r = 0.494$, $p < 0.01$), Zn ($r = 0.423$, $p < 0.05$), As ($r = 0.805$, $p < 0.01$), Cd ($r = 0.907$, $p < 0.01$), and Ba ($r = 0.809$, $p < 0.01$). It means higher straw concentrations of these heavy metals generate higher concentrations in rice grains.

Bioaccumulation and translocation factors

Although the significant correlations between the concentrations in different rice plant tissues and paddy soils can provide some interesting information on pathway of individual heavy metal, the transfer ability of heavy metals in the soil-rice system was still unclear. Therefore, BF and TF were employed to assess heavy metal accumulation from soil to root and heavy metal translocation in rice plant tissues, respectively. The descriptive statistical values of BFs and TFs of the heavy metals are summarized in Table 2. The bioaccumulation abilities of the heavy metals from paddy soil to rice root were in the ascending order of Ni < Cr ≈ Ba < Co < Cu < Zn ≈ Pb < Mn < Fe < < Cd < As. The BFs of As and Cd were significantly higher than other heavy metals. This can be attributed to relatively high concentrations of As and Cd accumulated in the rice root. Root is a main organ to retain As and Cd through chelation by phytochelatin, vacuolar compartmentalization, and adsorption (Nocito et al. 2011). Iron plaque also makes an important contribution to immobilization and sequestration of As and Cd in the roots (Liu et al. 2008, Liu et al. 2006). The transfer behaviors of the heavy metals in the rice plants were quite different from the BFs. The $TF_{r\text{-}s}$ and $TF_{s\text{-}g}$ were in the ascending order of Ba < Pb ≈ Cr < Mn < Co < Ni < Fe ≈ As < Cd < Zn < Cu and Fe < As < Pb < Co < Cd < Cu < Zn < Ba < Cr ≈ Ni < Mn, respectively. The $BF_{p\text{-}r}$ of Fe, Co, As, Cd, and Pb was higher than their $TF_{r\text{-}s}$ and $TF_{s\text{-}g}$, indicating that the rice roots transferred a small number of toxic elements such as As, Cd, and Pb to the aerial parts. The result is consistent with other published studies (Bhattacharya et al. 2010, Liu et al. 2013, Nocito et al. 2011). The $TF_{r\text{-}s}$ of Cr, Mn, Ni, and Ba was significantly higher than their $BF_{p\text{-}r}$ and $TF_{s\text{-}g}$. It means the translocation of these elements from the rice roots to the straws was efficient after uptake by the roots. However, the

Table 2 Descriptive data of BFs and TFs in the soil-rice system

Heavy metal		BFp-r	TFr-s	TFs-g
Cr	Mean ± SD	0.285 ± 0.156	1.43 ± 0.705	0.035 ± 0.056
	(min-max)	(0.126–0.783)	(0.250–2.73)	(0.001–0.275)
	CV	55%	49%	159%
Mn	Mean ± SD	0.959 ± 0.338	2.68 ± 1.68	0.049 ± 0.014
	(min-max)	(0.451–2.05)	(0.431–5.91)	(0.024–0.097)
	CV	35%	63%	28%
Fe	Mean ± SD	1.01 ± 0.462	0.008 ± 0.004	0.121 ± 0.080
	(min-max)	(0.337–.190)	(0.003–0.021)	(0.067–0.426)
	CV	46%	48%	67%
Co	Mean ± SD	0.345 ± 0.107	0.094 ± 0.038	0.067 ± 0.036
	(min-max)	(0.146–0.553)	(0.029–0.179)	(0.030–0.203)
	CV	31%	40%	53%
Ni	Mean ±SD	0.234 ± 0.134	1.43 ± 0.808	0.072 ± 0.080
	(min-max)	(0.083–0.772)	(0.330–3.11)	(0.006–0.395)
	CV	57%	56%	111%
Cu	Mean ± SD	0.457 ± 0.179	0.275 ± 0.096	1.33 ± 0.385
	(min-max)	(0.203–0.756)	(0.070–0.528)	(0.759–2.36)
	CV	39%	35%	29%
Zn	Mean ± SD	0.504 ± 0.162	0.831 ± 0.299	0.614 ± 0.180
	(min-max)	(0.243–0.909)	(0.347–1.57)	(0.339–0.988)
	CV	32%	36%	29%
As	Mean ± SD	7.26 ± 4.86	0.026 ± 0.012	0.122 ± 0.085
	(min-max)	(1.26–17.4)	(0.006–0.065)	(0.046–0.345)
	CV	67%	47%	69%
Cd	Mean ± SD	5.35 ± 3.89	0.183 ± 0.081	0.410 ± 0.132
	(min-max)	(0.480–13.0)	(0.060–0.351)	(0.135–0.677)
	CV	73%	44%	32%
Ba	Mean ± SD	0.286 ± 0.099	1.32 ± 0.547	0.016 ± 0.005
	(min-max)	(0.159–0.598)	(0.456–2.23)	(0.008–0.030)
	CV	35%	41%	32%
Pb	Mean ± SD	0.516 ± 0.308	0.050 ± 0.028	0.033 ± 0.027
	(min-max)	(0.253–1.60)	(0.013–0.126)	(0.004–0.126)
	CV	60%	57%	83%

transfer from the rice straws to the grain was restrained due to different cellular mechanisms (Hall 2002). Heavy metals stored in the straws were transported from the roots via the xylem and might be transported to the grains via the phloem (Yoneyama et al. 2010).

The correlations between $BF_{p\text{-}r}$ and $TF_{r\text{-}s}$, and $TF_{s\text{-}g}$ and $TF_{r\text{-}s}$ for individual heavy metal were investigated through fitting curve analysis. As illustrated in Fig. 2, the plots of all the heavy metals except Cd exhibit a similar variation tendency to decrease $BF_{p\text{-}r}$ and $TF_{s\text{-}g}$ associated with $TF_{r\text{-}s}$ increasing. This is correlated with heavy metal detoxification and stress tolerance in rice (Hall 2002). Plants have a range of potential cellular mechanisms for heavy metal detoxification which could increase the tolerance to heavy metal stress. These mechanisms included reduced uptake of heavy metals at the plasma membrane, chelation of heavy metals by phytochelatins, and segregation of heavy metals in the vacuole (Hall 2002, Nocito et al. 2011). For Cr and Zn, both $TF_{s\text{-}g}$ and $BF_{p\text{-}r}$ were decreased linearly with $TF_{r\text{-}s}$ increasing. For Mn, Fe, Co, Ni, Ba, and Pb, significant correlations were only observed between $TF_{r\text{-}s}$ and $TF_{s\text{-}g}$ or $BF_{p\text{-}r}$ and TFs-g in a linear or hyperbolic pattern. No significant relationship was observed between neither $BF_{p\text{-}r}$ and $TF_{r\text{-}s}$ nor $TF_{s\text{-}g}$ and $TF_{r\text{-}s}$ for Cu and As. However, the pattern of Cd was different from

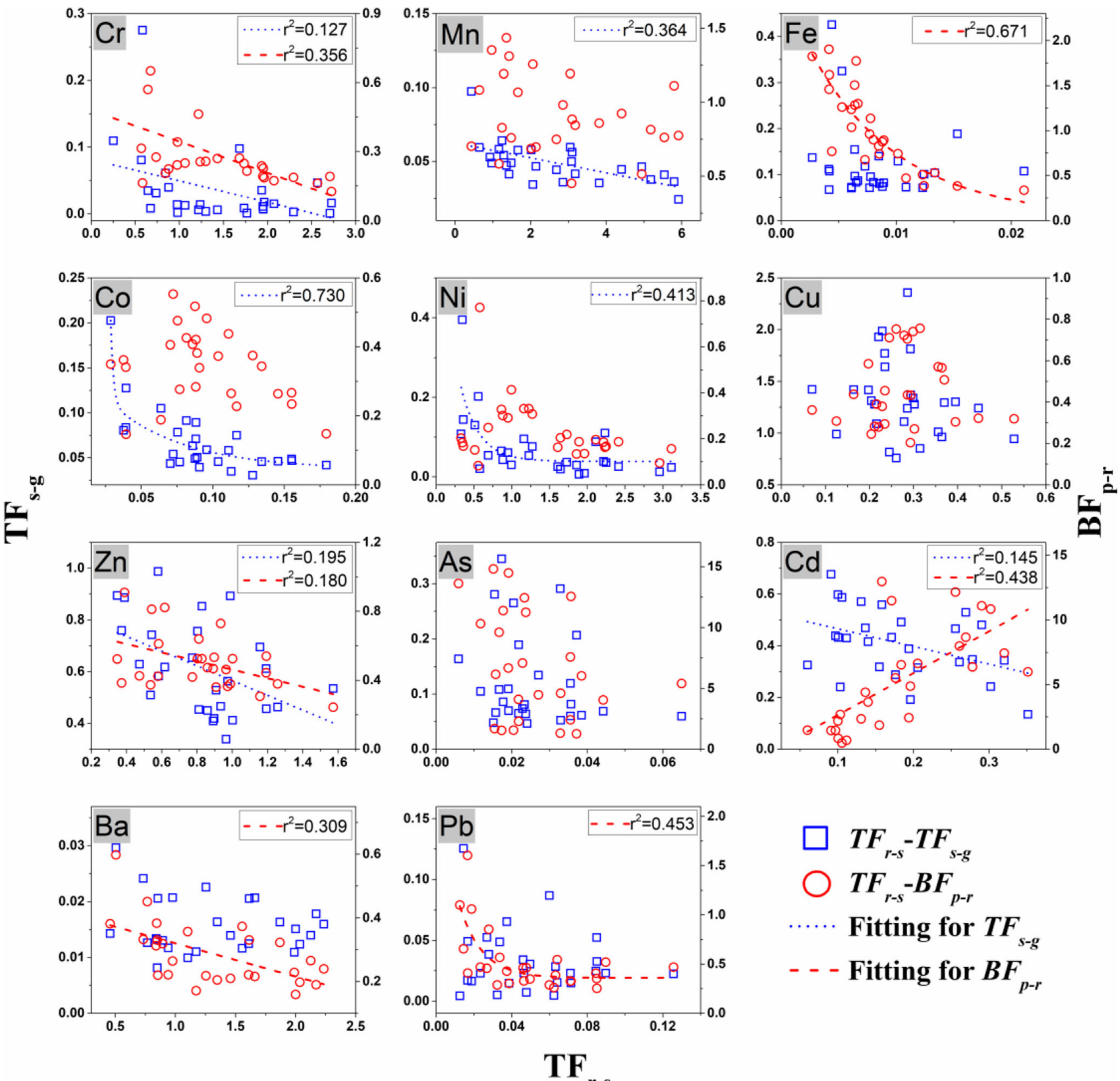

Fig. 2 Correlations between $TF_{r\text{-}s}$ and $BF_{p\text{-}r}$, $TF_{s\text{-}g}$ for individual heavy metal

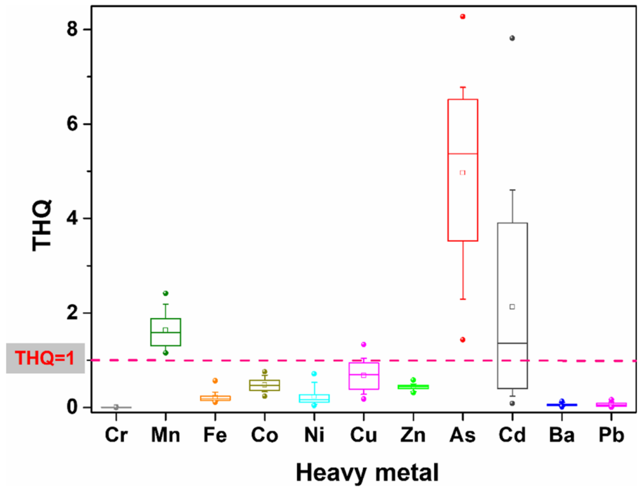

Fig. 3 Box plots of THQ for individual heavy metal. The square is the mean value. The circles in the bottom and top of box plots represented the minimum and maximum values, respectively. The bottom and top of the box are 25th and 75th percentile values, respectively. The horizontal lines in the bottom, middle and top of the box plot corresponded to 10th percentile, median and 90th percentile values, respectively

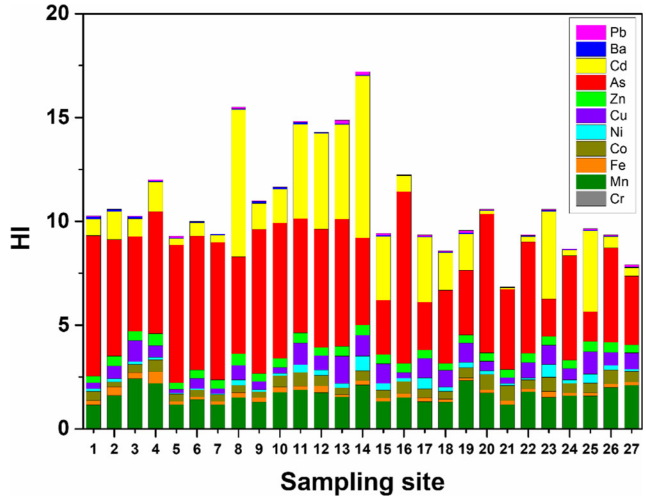

Fig. 4 Composition of HI for each sampling field near Changsha City

other heavy metals. The $TF_{s\text{-}g}$ for Cd was increased with $TF_{r\text{-}s}$ increasing. This might be on account of different pathway of toxic element Cd compared with nutritional elements such as Zn and Fe (Yoneyama et al. 2015).

Health risk assessment

The potential non-carcinogenic effects posed by chronic exposure to heavy metals via the rice were evaluated by THQ. There is no appreciable adverse effect on human health when the THQ is lower than the unit "1" as recommended by USEPA. As demonstrated in Fig. 3, the average THQ values of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba, and Pb were 0.002, 1.636, 0.211, 0.473, 0.228, 0.675, 0.431, 4.965, 2.131, 0.056, and 0.057, respectively. In this study, the average THQ values of Mn, As, and Cd exceeded "1," indicating considerable potential non-carcinogenic health risk to local inhabitants from rice consumption. Furthermore, the HI values were calculated to estimate overall risk in each sampling field. As shown in Fig. 4, the heavy metals As and Mn made important contributions to the HI in all the sampling fields. However, the THQ of Cd played a major role in some fields due to large variation of Cd concentrations in the rice grains. This can be attributed to different $TF_{r\text{-}s}$-$TF_{s\text{-}g}$ patterns and transport mechanisms mentioned before.

Conclusion

The distribution patterns of heavy metals including Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba, and Pb in the soil-rice system have been investigated using ICP-MS. For most heavy metals, the concentrations were in the ascending order of grain < straw < root < paddy soil with significant difference ($p < 0.05$). Root is a main organ to retain heavy metals especially As and Cd through chelation by phytochelatin, vacuolar compartmentalization, and adsorption. Relatively high contents of Cd and Pb (3.66 and 1.46 times higher than the threshold values, respectively) were observed in the paddy soils due to long-term mining and smelting processes of lead-zinc deposits in the upstream area. In the analyzed rice grain samples, 56% of As and 44% of Cd exceeded the Chinese maximum contaminant levels in rice indicating efficient transfer of both As and Cd from rice root to grain. Similar variation tendencies to decrease $BF_{p\text{-}r}$ and $TF_{s\text{-}g}$ associated with $TF_{r\text{-}s}$ increasing were observed for most of the heavy metals due to heavy metal detoxification and stress tolerance in rice. However, the $TF_{s\text{-}g}$ for Cd was increased with $TF_{r\text{-}s}$ increasing. This might be on account of different pathway of toxic element Cd compared with nutritional elements such as Zn and Fe. The average THQ values of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba, and Pb were 0.002, 1.636, 0.211, 0.473, 0.228, 0.675, 0.431, 4.965, 2.131, 0.056, and 0.057, respectively, indicating appreciable health risk to local consumers from exposure to Mn, As, and Cd in rice.

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