ORIGINAL ARTICLE

Modeling transfer of heavy metals in soil–rice system and their risk assessment in paddy fields

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Abstract Many studies have been conducted on model transfer in soil–plant systems. However, relatively little information is available on modeling metal transfer in soil–rice system and associated risk assessment in real paddy fields. Based on a random sampling method from Nanxun, Shengzhou and Wenling in Zhejiang province, China, 15 pairs of rice and the corresponding soil samples were respectively collected for analysis of heavy metals and soil pH. The results showed that the accumulation ability of rice for different heavy metals was significantly different ($p < 0.05$), and was in the order of Cd > Zn > Cu > Ni > Cr > Pb. The relationships of heavy metals in rice with those in soil, along with soil pH, were well described by linear regression models. Except for Pb, the contents of most metals in rice were positively correlated with those of the soil. Soil pH was negatively correlated with the contents of Cd, Zn and Ni in rice, and positively correlated with Pb in rice; however, it had less effect on Cr and Cu. Based on risk reference dose (R_fD), the risk assessment data indicated that the rice grown in Zhejiang paddy fields does pose some potential Cd and Cr contamination risk to food safety; rice in Shengzhou posed light Ni risk.

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Introduction

Food safety and the associated health risk is now one of the major concerns worldwide, especially in China. With the affiliation of China to the World Trade Organization (WTO), the quality of food has caught more attention by Chinese government, and green agriculture is becoming increasingly important. Among potential toxic pollutants, heavy metals are especially dangerous because of their non-biodegradability and persistence (Raghunath et al. 1999; Adriano 2001; Tembo et al. 2006). They can accumulate in the body through food chains, lead to psychotic disorders and cause many debilitating diseases (Coen et al. 2001; Lee et al. 2006). Therefore, heavy metals have attracted a great deal of attention worldwide and have been a focus of environmental studies (Adriano 2001; Li et al. 2004; Huang and Gobran 2005; Violante et al. 2008).

Rice is the dominant agricultural product in China and ranks second by quantity in the world. The quality of rice, thus, affects greatly human health. The Ministry of Agriculture of China has done a national survey on rice safety in 2002; the results revealed that rice has been contaminated by many heavy metals, such as Cd, Pb, Cr, Hg, As, Cu, and Zn. It was reported that 2.0×10^7 hm^2 paddy fields has been polluted by many heavy metals, which is 20% of the whole paddy field in China (Zhong et al. 2006). These metals may come from many pollution sources, such as excess use of agrochemical and fertilizer, sewage sludge disposal, and aerial fallout from industrial activities (Van-Camp et al. 2004). In addition, some studies on heavy metal concentrations of paddy fields in Zhejiang province,

China, were reported, indicating that the paddy soil in Zhejiang was polluted by metals to some extent, especially Cd and Ni (Liu et al. 2006; Shi et al. 2007). The transfer of heavy metals in the soil–rice system turns out to be a key problem for evaluating uptake of pollutants (US Environmental Protection Agency 1993; Dudka and Miller 1999). Much work has been carried out to reliably estimate the plant availability of heavy metals and predict their uptake by plants (Li et al. 1998).

Substantial research has been carried out to investigate the absorption, translocation, distribution of heavy metals in rice and the mechanisms involved, on the basis of pot experiments. There were significant variations between genotypes (Cheng et al. 2005; Li et al. 2005). Most research showed that the absorption ability of hybrid rice was higher than that of indica rice. The contents of heavy metals in rice were in the order root > stem > leaf > grain (Liu et al. 2003). They were correlated with soil pH (Reddy and Patrick 1977), and the concentrations were highest at pH 4.5–5.5 (Bingham et al. 1980; Kitagishi and Ramane 1981). Besides pot experiments, previous studies carried out in the laboratory was mainly focused on some special regions and contaminated environments, such as mine region (Jung and Thornton 1997; Fazeli et al. 1998; Liu et al. 2005), and roadside farmland (Zhang et al. 2005). Chen et al. (2001) suggested that the absorption characterization of heavy metals in rice varied with concentrations of heavy metals in soils and different pollution sources. Up to now, little work was conducted in real paddy fields.

The objectives of this study were: (1) to investigate the accumulation of heavy metals in soil–rice system in paddy fields, (2) to study the correlation between the heavy metal contents of the paddy soils and those of rice based on a good prediction model, and (3) to assess the associated health risk and environmental quality.

Materials and methods

Study area and sampling

The research was conducted in the province of Zhejiang (118°–123°E, 27°–31°30′N), located in southeast China. The agriculture in Zhejiang province is quite well developed, especially in rice production. Zhejiang province is one of main rice production regions in China, and is one of the most industrialized provinces. Due to rapid industrialization, the heavy metal pollution in paddy fields in Zhejiang province is of increasing concern. The specific study areas included Nanxun city (120°4′–120°29′E, 30°38′–30°56′N), Shengzhou city (120°28′–121°7′E, 29°20′–29°50′N) and Wenling city (121°10′–121°44′E, 28°13′–28°32′N), which are located in the north, middle and southeast Zhejiang province, respectively (Fig. 1). They are not only representative rice production areas, but also highly industrialized areas in Zhejiang and southeast China. Zhejiang in this paper refers to the whole of the three studied cities, Nanxun, Shengzhou and Wenling.

At the harvest time (October 2006), 15 samples were collected from each of the paddy fields from Nanxun, Shengzhou and Wenling, respectively, by means of a random sampling method, on the basis of a land use map at 1:50,000 scale. Each sample was the composite of at least five sub-samples. The rice and their rooted soil samples

Fig. 1 Sketch map of the study regions and samples
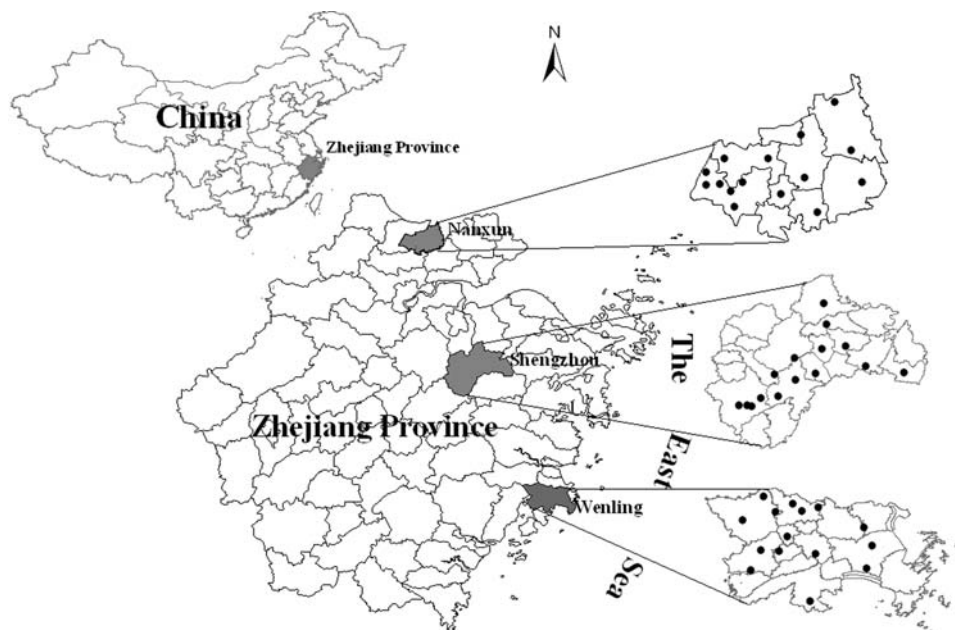
(at 0–15 cm in depth) were collected from each site. The coordinates of sampling locations were recorded with a differential global position system (GPS). Sampling was focused in plain rice production regions, and mountainous areas around Shengzhou and some in Wenling were avoided (Fig. 1).

Chemical analysis

Soil samples were air-dried in the laboratory for several days at ambient temperature. They were passed through a 2 mm nylon sieve for a general analysis of soil properties. Then some of the soil samples were ground to pass through 100 meshes and stored in closed polyethylene bags for heavy metal content analysis.

Rice samples were oven-dried at 105°C for 1 h, then at 70°C to constant weight. Hull was removed from rice. Then rice samples were comminuted using a pulverizer, ground to pass through 100 meshes using a nylon sieve and stored in closed polyethylene bags for further analysis.

Heavy metals both in the soil and rice samples were analyzed according to the national standard methods in China (Agricultural Chemistry Committee of China 1983). The heavy metal concentrations of soil samples, with the exception for Cd, were determined by flame-atomic absorption spectroscopy (FAAS) following $HF–HNO_3–HClO_4$ digestion procedures. The heavy metal concentrations of rice samples and Cd of soil samples were determined with graphite furnace atomic absorption spectroscopy (GFAAS) following $HNO_3–HClO_4$ (4:1) digestion procedures for rice samples and $HF–HNO_3–HClO_4$ digestion procedures for soil samples. The Hg concentration was determined by cold vapor atomic fluorescence spectroscopy following $HNO_3–H_2SO_4$ procedure. Soil pH was measured at a 1:2.5 soil:water ratio in an aqueous suspension (Agricultural Chemistry Committee of China 1983). Soil organic matter was determined by the potassium dichromate wet combustion procedure (Agricultural Chemistry Committee of China 1983). Cation exchange capacity was measured according to the procedure of Hendershot and Duquette (1986). Soil total nitrogen was measured by Kjeldahl method. Soil available phosphorus was extracted by using 0.5 M $NaHCO_3$ (pH 8.5) and phosphorus concentration in the extract was determined by using the molybdenum-blue method (Agricultural Chemistry Committee of China 1983). Soil available potassium was extracted using NH_4OAc and then measured by flame emission spectrometry (Agricultural Chemistry Committee of China 1983).

Statistical analysis

The basic statistics, the tests for normality and correlation significance, and multivariate regression analysis were performed using SPSS 13.0 for windows. The location and sample map was produced using ArcGIS 9.0 software. All data were made normal transfer prior to tests of significance and regression analysis. The data of Zhejiang in this paper were the average values of the respective heavy metals obtained from the three studied regions.

Results and discussion

Concentrations of metals in soil and rice

Contents of metals in the paddy soils are shown in Table 1. The metal contents were variable in different areas of Zhejiang. The mean contents for Cd, Pb, Cu and Zn in Wenling were higher than those in other two cities, while that for Cr and Hg were highest in Nanxun. The metal contents were apparently related to the extent of industrialization; Wenling is relatively more industrialized. Previous studies reported that Cd pollution was distributed in industrialized regions, especially with plating, dye, batteries and electric machines producing industries (Liu 2006). The leather industry may be the main source for the accumulation of Cr and Hg in Nanxun soil.

Metal contents in rice are shown in Table 2. The content for Hg was below the detection limit. The mean contents for Cd and Zn were highest in Wenling; those for Cr and Pb were highest in Nanxun and those for Cu and Ni were highest in Shengzhou.

One way to evaluate environmental pollution is to compare the values of the metal contents of the samples with reference values. In this study, the environmental quality for soil in China (Ministry of Environmental Protection of China 1995), and maximum levels of contaminants in foods in China (Ministry of Health of China 2005) were used as the basis for the threshold values for heavy metal pollution in soil and rice, respectively. The percentages of samples for each metal exceeding the threshold values are also shown in Tables 1 and 2. Table 1 shows that the soils in Zhejiang province were contaminated by Cd, Ni and Hg to some extent. The pollution by Cu and Zn were relatively low; the contents of Cr and Pb of the studied soils were all below the threshold values. Soil in Wenling was contaminated by most metals to different degree, except for Cr and Pb. It can also be observed (Table 2) that the rice in Zhejiang was contaminated by Cd, Cr and Pb to some degree, however, the rice was nearly safe for Cu and Zn. Similar to the soil contamination, the Cd contamination of the rice in Wenling was higher than that in other two cities, and Cd contamination was higher than that of other metals indicating Cd as one of the main pollutants.

Table 1 Contents of heavy metals in soils from different areas in Zhejiang province (mg kg⁻¹)

Study area	Cd		Cr		Hg		Pb		Cu		Zn		Ni	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
Shengzhou	0.11 ± 0.06	0.00–0.20	29.8 ± 18.9	15.1–78.1	0.12 ± 0.04	0.07–0.23	34.3 ± 8.1	22.0–50.4	19.8 ± 8.0	11.9–39.1	75.8 ± 19.2	34.7–113.6	19.2 ± 17.8	5.1–62.7 (20)
Nanxun	0.14 ± 0.06	0.09–0.24	45.1 ± 5.8	37.0–55.7	0.25 ± 0.11	0.14–0.60 (13)	31.1 ± 3.7	24.9–40.1	25.6 ± 4.4	18.8–33.9	92.7 ± 14.2	77.8–126.5	23.9 ± 5.2	14.3–32.9
Wenling	0.22 ± 0.11	0.08–0.40 (33)[c]	36.1 ± 15.7	9.5–55.1	0.18 ± 0.08	0.08–0.41 (6.5)	48.3 ± 26.5	27.0–140.0	32.3 ± 10.3	14.8–52.8 (6.5)	143.4 ± 127.0	65.9–594.5 (6.5)	23.8 ± 13.0	5.6–54.9 (6.5)
Zhejiang[a]	0.16 ± 0.09	0.04–0.40 (11)	36.9 ± 15.6	9.5–78.1	0.18 ± 0.10	0.07–0.60 (6.5)	37.9 ± 17.5	22.0–140.0	25.9 ± 9.3	11.9–52.8 (2.2)	104.0 ± 78.4	34.7–594.5 (2.2)	22.3 ± 13.0	5.1–62.7 (8.8)
Threshold value[b]	0.3		250		0.3		250		50		200		40	

[a] The data of Zhejiang in this paper are the average values of the respective heavy metals obtained from the three studied regions

[b] Used as the benchmark of soil contamination recommended by Ministry of Environmental Protection of China (1995)

[c] The data within a parenthesis stands for the percent of samples exceeding the Environmental Quality Standard for Soil in China (Ministry of Environmental Protection of China 1995)

Table 2 Contents of heavy metals in rice from different areas in Zhejiang province (mg kg⁻¹)

Study area	Cd		Cr		Pb		Cu		Zn		Ni		Hg	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
Shengzhou	0.07 ± 0.05	0.00–0.20	0.22 ± 0.34	0.04–1.45 (6.5)	0.08 ± 0.03	0.05–0.15	3.2 ± 0.9	1.3–4.7	23.5 ± 2.8	18.5–27.8	0.41 ± 0.33	0.12–1.46	ND	ND
Nanxun	0.01 ± 0.01	0.00–0.03	0.34 ± 0.20	0.09–0.72	0.11 ± 0.03	0.06–0.21 (6.5)	2.3 ± 0.6	1.2–3.4	16.6 ± 2.3	12.7–21.6	0.10 ± 0.07	0.01–0.25	ND	ND
Wenling	0.14 ± 0.15	0.00–0.44 (33)[c]	0.24 ± 0.10	0.13–0.50	0.08 ± 0.03	0.02–0.14	3.0 ± 1.0	0.7–4.3	25.5 ± 6.1	15.8–38.5	0.25 ± 0.23	0.02–0.91	ND	ND
Zhejiang[a]	0.07 ± 0.11	0.00–0.44 (11)	0.27 ± 0.24	0.04–1.45 (2.2)	0.09 ± 0.04	0.02–0.21 (2.2)	2.8 ± 0.9	0.7–4.7	21.9 ± 5.5	12.7–38.5	0.25 ± 0.27	0.01–1.46	ND	ND
Threshold value[b]	0.2		1		0.2		10		50		nd[d]		0.02	

ND not detectable

[a] The data of Zhejiang are the average values of the respective heavy metals obtained from the three studied regions

[b] Used as the benchmark of rice contamination recommended by Ministry of Health of China (2005)

[c] The data within a parenthesis stands for the percent of samples exceeding Maximum Levels of Contaminants in Foods in China (Ministry of Health of China 2005)

[d] nd means the threshold value is not defined by Ministry of Health of China (2005)

Compared with other metals in soils (Table 1), the main metal pollutants of rice (Table 2) were not in accordance with those of soils. The variation of the heavy metal contents in the studied paddy soils was not the same as that in rice. Therefore, it is suggested that the accumulation difference between heavy metals for rice may exist, and besides the contents of total heavy metals of the soils, the absorption may be affected by other factors.

Metals in soil–rice system

In order to understand the accumulation difference for heavy metals in rice, enrichment index was determined (Table 3), which was defined as the metal concentration in rice divided by that in soil. Enrichment index provides a useful indication of the metal availability from soil to plants (Lee et al. 2001). Table 3 shows that the absorption and accumulation of heavy metals in rice varied significantly ($p < 0.05$) with the types of metals in some soils. The values for Cd, Zn and Cu were much higher than those for Pb, Cr and Ni. The accumulation ability for metals was generally in the order of Cd > Zn > Cu > Ni > Cr > Pb. However, the different enrichment index values of the same metal was observed between the studied areas, indicating that heavy metal availability to rice may be affected by soil physical, chemical and biological properties besides the total metal content of the soils.

Many researchers have investigated factors influencing metals uptake by rice, which include soil pH (Reddy and Patrick 1977; Dutta et al. 1989), organic matter (Haldar and Mandal 1979; Kashem and Singh 2001), redox potential (Sajwan and Lindsay 1986), salinity (McLaughlin et al. 1994), phosphorous content (Haldar and Mandal 1981). Soil pH is the significant factor ($p < 0.01$) controlling uptake of heavy metals (Tang 2007), and above all, is the most important factor (Jung and Thornton 1997; Basta et al. 2005). The soil properties in the study areas are shown in Table 4.

In Table 3, the values for Cu, Zn and Ni in Shengzhou city were significantly higher ($p < 0.05$) than those in other two study areas. The data indicate that the soil properties (Table 4) in Shengzhou is easier to lead to accumulation of these heavy metals in rice, and may have higher potential risk, since the pH, organic matter content, and CEC values were lower than those of the other two soils.

The correlations between heavy metals in the paddy soils and rice were shown in Fig. 2. Among the studied metals, only the contents of soil Cd and Zn were significantly ($p < 0.01$) correlated with those in rice. For most heavy metals studied, Fig. 2 shows that there is no significant correlation between the concentrantion of heavy metal in soil and those in rice. So it indicates that the total

**Table 3** Enrichment index values of heavy metals in rice from different areas

Study area	Cd		Cr		Pb		Cu		Zn		Ni	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range
Shengzhou	0.588 ± 0.344 a	0.094–1.293	0.011 ± 0.024 a	0.001–0.096	0.002 ± 0.001 a	0.001–0.004	0.174 ± 0.068 a	0.073–0.303	0.339 ± 0.143 a	0.219–0.764	0.028 ± 0.017 a	0.008–0.062
Nanxun	0.077 ± 0.065 b	0.030–0.282	0.008 ± 0.004 a	0.002–0.015	0.004 ± 0.001 b	0.002–0.005	0.093 ± 0.035 b	0.038–0.153	0.185 ± 0.045 b	0.115–0.273	0.005 ± 0.005 b	0.000–0.017
Wenling	0.617 ± 0.709 a	0.013–2.435	0.009 ± 0.006 a	0.002–0.020	0.002 ± 0.001 a	0.000–0.005	0.097 ± 0.034 b	0.048–0.154	0.221 ± 0.085 b	0.065–0.401	0.014 ± 0.017 c	0.002–0.062
Zhejiang[a]	0.427 ± 0.512 A	0.013–2.435	0.009 ± 0.014 D	0.001–0.096	0.003 ± 0.001 D	0.000–0.005	0.121 ± 0.060 B	0.038–0.303	0.248 ± 0.118 C	0.065–0.764	0.016 ± 0.017 D	0.000–0.062

Different lower case letters in the same column and different capital letters in the same row mean significantly different at the 0.05 level

[a] The data of Zhejiang are the average values of the respective heavy metals obtained from the three studied regions

Table 4 The physical and chemical properties of the paddy soil in Zhejiang province (mean ± SD)

Study area	pH (range)	Organic matter content (%)	Cation exchange capacity (cmol kg^{-1})	Total nitrogen (%)	Available phosphorus (mg kg^{-1})	Available potassium (mg kg^{-1})
Shengzhou	3.88–7.03	2.93 ± 0.84	12.98 ± 6.07	0.19 ± 0.07	19.42 ± 36.16	100.06 ± 31.41
Nanxun	4.19–8.02	3.37 ± 1.25	17.06 ± 3.02	0.18 ± 0.06	27.48 ± 47.40	96.43 ± 41.42
Wenling	4.41–8.93	3.03 ± 1.16	18.01 ± 2.51	0.25 ± 0.12	34.20 ± 51.24	218.00 ± 73.84
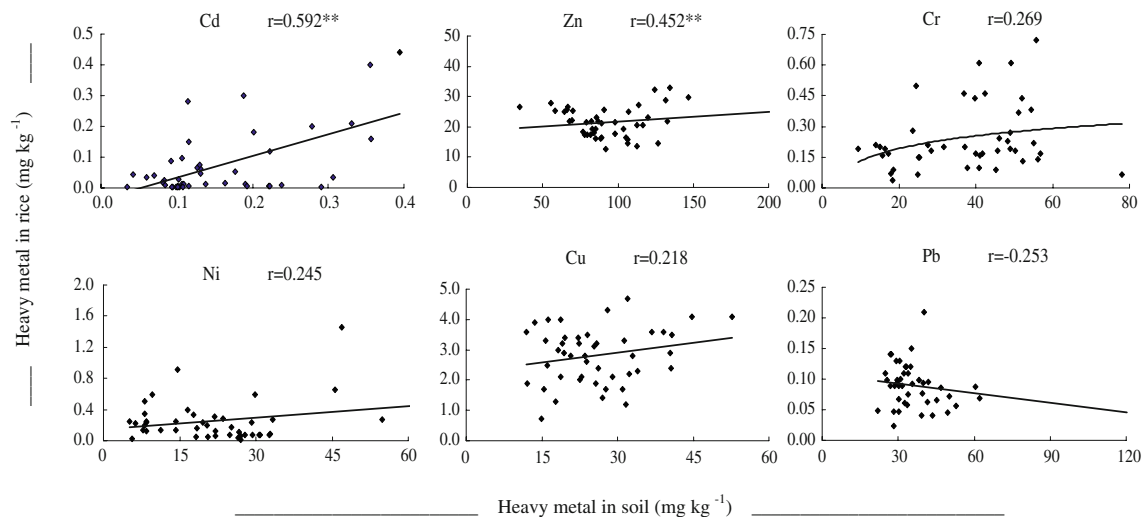
Fig. 2 Relationship between heavy metals in the paddy soils and in rice

heavy metal concentrations alone in soil cannot reliably estimate the availability of most of heavy metals to rice.

Modeling transfer for metals in soil–rice system

Based on the previous research about factors influencing metals uptake by rice as discussed in "Metals in soil–rice system", in this paper, the best-fit models for predicting the heavy metals contents in rice was developed based on soil properties in paddy soil–rice system in the study area, using multiple regression analysis which included soil pH and heavy metal contents only. The concentration values of Cd and Cr in rice and those of Cd, Pb, Cr and Cu in soils were logarithmically transformed to normalization. The multiple regression equations are shown in Table 5.

The concentrations of Cd, Zn, Pb and Ni in rice were correlated significantly at the 0.01 level ($p < 0.01$) to the metal concentration and pH of the soils, while the concentrations of Cu and Cr in rice were significantly correlated at the 0.05 level ($p < 0.05$) to the metal concentrations in the soils. The equations for Cd, Zn, Pb and Ni including the heavy metal content in soil only were also shown in Table 5. Comparing the R and r values, the regression equations including the metal concentration of the soil and soil pH, can better predict the contents of Cd,

Zn, Pb and Ni in rice than those based on the soil heavy metal concentration alone. However, in the regression equations for Cu and Cr including metal concentration in soil and soil pH, the partial coefficients between the metal concentration in rice and soil pH were not significant (Table 5), indicating that the availability of Cu and Cr to rice were not significantly affected by soil pH in the paddy field. Therefore, the best prediction models for Cu and Cr are the regression equations based on the metal concentration of the soils. The concentrations of most heavy metals in rice were positively correlated with those in the soils, except that the negative correlation was observed between Pb in rice and that in the soils. Cd, Zn and Ni in rice were negatively correlated with soil pH, and Pb was positively correlated with soil pH. Liu et al. (2005) revealed that the metal accumulation effect strongly depends on the crop's physiological properties and the availability of metals in soils. The high concentration of Pb in soil would lead to the decline of the chlorophyll content in rice plant, and the accumulation of the rice proline and peroxidase, which result in damaging the rice plant and restrain the absorption of Pb (Zeng et al. 2007). This negative correlation may also be attributable to the transformation of Pb to less available forms with the increase of Pb accumulation in the soils. However, different

Table 5 Correlation models for heavy metals in paddy soil–rice system in Zhejiang province ($n = 45$)

Metals	Model	Model		Partial correlation coefficient	
		R	r	Metal in soil	Soil pH
Cd	$Log\ Cd_{rice} = 0.8982Log\ Cd_{soil} - 0.3534pH + 1.2055^a$	0.518**	–	0.335*	−0.364**
	$Log\ Cd_{rice} = 1.1327Log\ Cd_{soil} - 0.6207$	–	0.395**	0.395	–
Zn	$Zn_{rice} = 0.0312Zn_{soil} - 3.3887pH + 38.0919^a$	0.611**	–	0.487**	−0.461**
	$Zn_{rice} = 0.0319Zn_{soil} + 18.5566$	–	0.452**	0.452**	–
Pb	$Pb_{rice} = -0.0834Log\ Pb_{soil} + 0.0131pH + 0.1409^a$	0.468**	–	−0.298*	0.285*
	$Pb_{rice} = -0.1101Log\ Pb_{soil} + 0.2573$	–	−0.387*	−0.387*	–
Ni	$Ni_{rice} = 0.0035Ni_{soil} - 0.1133pH + 0.7811^a$	0.444**	–	0.273*	−0.427**
	$Ni_{rice} = 0.0050Ni_{soil} + 0.1419$	–	0.245	0.245	–
Cr	$Log\ Cr_{rice} = 0.4673Log\ Cr_{soil} - 1.4075^a$	–	0.347*	0.347*	–
	$Log\ Cr_{rice} = 0.4026LogCr_{soil} + 0.0434pH - 1.5573$	0.360	–	0.275	0.101
Cu	$Cu_{rice} = 2.3905Log\ Cu_{soil} - 0.5761^a$	–	0.391*	0.391*	–
	$Cu_{rice} = 2.3736Log\ Cu_{soil} + 0.0215pH - 0.6758$	0.391*	–	0.384*	0.018

–, not applicable

*Significant at the 0.05 level

**Significant at the 0.01 level

[a] The best-fit correlation model for the respective metal in the paddy soil–rice system

relationship between pH and the availability of Pb was reported in previous studies. Reddy and Patrick (1977) reported that the availability of Pb decreased with an increase in pH; Dayton et al. (2006) reported that there was no significant pH effect on the availability of Pb. Therefore, the pH effect on the availability of soil Pb appears to be a controversial issue.

Dudka et al. (1996) reported that the relationship of heavy metals in rice and soil could be described by three models: linear (constant partitioning model), plateau (saturation model), and Langmuir sorption model. The linear model may also occur at a low range of metal concentrations in soils. In the present study, the metal concentrations in soil samples, which were collected from the paddy fields, were generally low. Therefore, the linear models were applicable as shown in Table 5.

The R or r values for the best-fit models ranged from 0.347 to 0.611 (Table 5). However, higher coefficients were reported in previous studies. Dudka et al. (1996) reported that the r values for the correlation of the concentration of Cd and Zn in barley grain with those in soil were 0.94 and 0.92, respectively. The similar correlation coefficients were found by McBride (2002). Correlation coefficients in this study were lower than previous works (usually $r > 0.9$). However, the previous researches mentioned above were performed by pot experiments or small

Table 6 Potential risk assessment of rice in paddy field in Zhejiang province

Study area	Sample number	Cd			Cr			Pb			Cu			Zn			Ni		
		Range mg kg^{-1}	N^c	%^{d}	Range (mg kg^{-1})	N	%	Range (mg kg^{-1})	N	%	Range (mg kg^{-1})	N	%	Range (mg kg^{-1})	N	%	Range (mg kg^{-1})	N	%
Shengzhou	15	0.00–0.20	7	46.7	0.04–1.45	2	13.3	0.05–0.15	nd	nd	1.3–4.7	nd	nd	18.5–27.8	0	0	0.12–1.46	1	6.7
Nanxun	15	0.00–0.03	0	0	0.09–0.72	4	26.7	0.06–0.21	nd	nd	1.2–3.4	nd	nd	12.7–21.6	0	0	0.01–0.25	0	0
Wenling	15	0.00–0.44	8	53.5	0.13–0.50	5	33.3	0.02–0.14	nd	nd	0.7–4.3	nd	nd	15.8–38.5	0	0	0.02–0.91	0	0
Zhejiang^a	45	0.00–0.44	15	33.3	0.04–1.45	11	24.4	0.02–0.21	nd	nd	0.7–4.7	nd	nd	12.7–38.5	0	0	0.01–1.46	1	2.2
Maximum tolerable concentrations^b (mg kg^{-1})		0.089			0.159			nd^e			nd			159			1.064		

[a] The data of Zhejiang are the average values of the respective heavy metals obtained from the three studied regions

[b] The data was estimated based on R_fD value recommended by US Environmental Protection Agency (2006)

[c] The number of samples exceeding the maximum tolerable concentrations

[d] The percent of samples exceeding the maximum tolerable concentrations

[e] nd means the R_fD value is not defined by US Environmental Protection Agency (2006)

field experiments, so there was less variation among soil properties in modeling. Furthermore, soils in paddy fields are a complicated system. Besides soil total metal contents and pH, other soil properties may also play some role on influencing the availability of heavy metals in rice, which would weaken the fit of models including soil metal and pH only.

Risk assessment

Risk assessment of rice produced in Zhejiang province were conducted with risk reference dose (R_fD) recommended by US Environmental Protection Agency (2006) as benchmark. The R_fD values are 0.0005, 0.003, 0.02 and 300 mg kg^{-1} per day for Cd, Cr, Ni and Zn, respectively. The consumption of rice grain in China is 206 kg per year per person, and as much as 50% of food intake may be assumed to come from contaminated soil (Dudka et al. 1996). So the consumption of the rice coming from contaminated fields is 0.282 kg per day per person. Based on the above assumption, the maximum tolerable concentrations of heavy metals in rice can be estimated (Table 6). The risk assessment results are shown in Table 6. All the study areas showed some Cr risk. Cd risk was observed in Wenling and Shengzhou, and light Ni risk was observed in Shengzhou. Generally, rice grown in Zhejiang paddy fields does pose some potential Cd and Cr risk to food safety and human health. In order to guard food safety, one should take positive measures to control paddy soil pollution and improve the environmental quality.

Conclusions

Among the heavy metals studied, Cd in the paddy soils had the highest availability for uptake by rice plant, and the availability of heavy metals to rice plant was in the order of Cd > Zn > Cu > Ni > Cr > Pb. Soil is a complicated system and the interactions between rice plant and soil are intricate. The predicting models developed in this study, including total heavy metals and pH of the soil, can significantly describe the transfer of most heavy metals in the paddy soil–rice system. The concentrations of most heavy metals studied in rice were positively correlated with those in the soils, while the negative correlation existed between Pb in rice and that in the soils. The concentrations of Cd, Zn, Ni and Pb in rice were significantly effected by the soil pH; however, Cu and Cr concentrations in rice were less effected.

Due to rapid soil pollution, the rice in Zhejiang has potential Cd and Cr risk which could pose threat to human health because of long term consumption of these rice grains. The rice in Shengzhou has light Ni risk. Positive measures should thus be taken in account to control paddy soil pollution and to curtail metal contamination to the food chain.

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