



## Occurrence of arsenic in brown rice and its relationship to soil properties from Hainan Island, China

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### ABSTRACT

The acquaintance of arsenic concentrations in rice grain is vital in risk assessment. In this study, we determined the concentration of arsenic in 282 brown rice grains sampled from Hainan Island, China, and discussed its possible relationships to the considered soil properties. Arsenic concentrations in the rice grain from Hainan Island varied from 5 to 309  $\mu\text{g}/\text{kg}$ , with a mean (92  $\mu\text{g}/\text{kg}$ ) lower than most published data from other countries/regions and the maximum contaminant level (MCL) for  $\text{As}_i$  in rice. The result of correlation analysis between grain and soil properties showed that grain As concentrations correlated significantly to soil arsenic speciation, organic matter and soil P contents and could be best predicted by humic acid bound and Fe–Mn oxides bound As fractions. Grain arsenic rises steeply at soil As concentrations lower than 3.6  $\text{mg}/\text{kg}$  and gently at higher concentrations.

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### 1. Introduction

The transfer of arsenic from paddy soil to rice is a major exposure route of this highly toxic element to humans. Rice is the staple food for around 50% of the world's population, contributing over 70% of the energy and 50% of protein provided by their daily food intake (IRRI, 1993). In addition, arsenic is readily assimilated by rice plants due to flooding of paddy soil and the subsequent increasing of arsenic mobility (Heikens, 2006). Rice grain baseline levels of As are generally  $\sim 10$ -fold higher than other cereal grains (Williams et al., 2007). The studies from Bengal indicated that rice contributed about 50% to the total arsenic intake (Signes-Pastor et al., 2008). Total dietary studies in Europe and the United States show that rice is the primary source of As in a nonseafood diet (Schoof et al., 1999; Robberecht et al., 2002; Tao and Bolger, 1999).

The acquaintance of arsenic concentrations in rice grain is vital in risk assessment. Zavala and Duxbury (2008) reported a global normal range of 0.08–0.20  $\text{mg}/\text{kg}$  for arsenic concentration in rice. Meharg et al. (2009) analyzed 901 polished grain samples from 10 countries from 4 continents. They found median total arsenic concentrations of rice varied 7-fold, with Egypt (0.04  $\text{mg}/\text{kg}$ ) and

India (0.07  $\text{mg}/\text{kg}$ ) having the lowest arsenic concentration while the U.S. (0.25  $\text{mg}/\text{kg}$ ) and France (0.28  $\text{mg}/\text{kg}$ ) having the highest concentration. In recent years, brown rice and rice bran based foods are increasingly being identified as “Health food”, as they are high in antioxidants, vitamins, mineral nutrients, and soluble fiber (Sun et al., 2008; Zhu et al., 2008b). With respect to healthy effects on Human, brown rice or rice bran also contains high levels of toxic compounds, especially arsenic (Zhu et al., 2008b; Meharg et al., 2008; Sun et al., 2008). Zhu et al. (2008b) demonstrated that tacking and solving dietary exposure to inorganic As ( $\text{As}_i$ ) at the rice source is feasible. Pragmatically, for countries largely dependent on rice imports, low  $\text{As}_i$  rice can be sourced from appropriate regions. Therefore, more data about As in rice (both white and brown rice) should be collected, especially those from less polluted areas.

Hainan Island, located in the southernmost of China, is one of the least polluted regions in China. In this study, 282 brown rice samples were collected throughout the Hainan province to determine their As concentrations. Arsenic uptake and translocation in rice plants are affected by a wide range of factors including soil arsenic speciation, soil physical and chemical properties, irrigation water, and fertilizer management (Brammer, 2009; Zhao et al., 2009; Lu et al., 2009; Norton et al., 2009). Therefore, we also discussed the possible relationships between rice arsenic concentration and soil arsenic speciation and some basic soil properties (pH, organic matter, P and Si contents) for the purpose of determining

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whether there is a dominant factor in controlling the grain As concentrations.

## 2. Materials and methods

### 2.1. Sample collection and preparation

The study area, Hainan Island, is located in the southernmost China ( $18^{\circ}10'–20^{\circ}10'N$ ,  $108^{\circ}37'–111^{\circ}03'E$ ) and covers 33,920 km<sup>2</sup> of land area (Fig. 1). Climate in this area is tropical monsoon with average annual rainfall of 1600–2500 mm and average annual temperature of 23–25 °C. The area of paddy fields in this province reached 350,000 ha. Most of the studied paddy soils were derived from clastic sediments, acid igneous rocks and basalt, few from metamorphic rocks. Brown rice grain samples (cultivar bollyou15, *Oryza sativa* L.), including 141 early rice and 141 late rice, were taken from 141 fields throughout the Hainan province in 2008 (Fig. 1). Each sample was taken from 4–5 random points of a field and merged to a composite sample. From each point 20 plants were harvested. The soil samples were collected just from the root zone of the early rice plants at harvest. So the correlation discussed below was limited to between the early rice and soil.

Rice samples were oven dried (~60 °C), and then the grains were separated by hand and milled to powder by a ball mill. Soil samples were air dried, and crushed to pass through a 0.85 mm nylon sieve (20 mesh). The sub-samples were then ground with an agate grinder to <0.15 mm (100 mesh).

### 2.2. Analytical methods

Soil pH was determined in a 2.5:1 water/soil suspension using a pH meter (LY/T 1239-1999). Soil organic matter (OM) content was determined by potassium dichromate method (LY/T 1237-1999). Soil available silica was determined by the extraction with NaOAc (LY/T 1266-1999). Soil available P was determined by the extraction with HCl and NH<sub>4</sub>F (LY/T 1233-1999). For total element determination of the soil, 0.25 g soil sample was weighed into a 50-ml Teflon vessel. Concentrated HCl (5 ml), HNO<sub>3</sub> (5 ml), HF (4 ml), and HClO<sub>4</sub> (2 ml) were then added and heated on a hot plate until near dryness. After cooling, the residue was redissolved in 2 ml concentrated HNO<sub>3</sub>. The digest was transferred into a 50-ml volumetric flask, mixed with 5 ml of sulphurea solution (50 g/L), and diluted to mark with Milli-Q water. For rice analysis, 1.0 g grain powder was weighed into a 100-ml Erlenmeyer flask, then added 8 ml concentrated HNO<sub>3</sub> and 2 ml concentrated HClO<sub>4</sub>. After reaction overnight, the flask was heated on a hot plate until the solution became transparent or yellowish. After digestion, the digest was transferred into a 25-ml volumetric flask, then added 2.5 ml of sulphurea solution (50 g/L) and diluted to mark.

The arsenic speciation in the paddy soils was assessed using a sequential extraction procedure modified from Tessier et al. (1979). This method has been validated and recommended by China Geological Survey (CGS, 2005) which divided the elements into six phases: F1, exchangeable fraction (2.5 g soil extracted by 25 ml of 1 M MgCl<sub>2</sub>, pH = 7.0, for 20 min); F2, carbonate bound fraction (1 M NaOAc adjusted to pH = 5.0 with acetic acid, for 6 h); F3, humic acids (HA) bound fraction (0.1 M Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, pH = 10.0, for 3 h); F4, Fe–Mn oxides bound fraction (0.04 M

NH<sub>2</sub>OH·HCl in 25% (v/v) HOAc at 96 °C, for 6 h); F5, organic matter and sulfides bound fraction (5 ml of 30% H<sub>2</sub>O<sub>2</sub> and 3 ml of 0.02 M HNO<sub>3</sub> for 2 h, a second 3 ml of 30% H<sub>2</sub>O<sub>2</sub> for 3 h, at 85 °C); F6, residual fraction (total digestion with a concentrated mixture of HCl/HNO<sub>3</sub>/HF/HClO<sub>4</sub>).

Arsenic concentrations in all the prepared solutions were determined by hydride generation atomic fluorescence spectrometry (HG-AFS). P and Si of soil digested solution were measured by inductively coupled plasma optical emission spectrometer (ICP-OES). Total soil Si concentration was determined by X-ray fluorescence spectrometric (XRF) after the sample being further ground to ~75 μm (200 mesh).

### 2.3. Quality control

The sampling procedure and chemical analysis were performed according to the standard methods recommended by China Geological Survey (CGS, 2005). The element measurements were validated by certified reference materials (CRM) GBW 10010 (Chinese rice flour) and GBW 07415 (Chinese paddy soil). The average CRMs recovery for As ranged from 90 to 105%, for P and Si it was 95–100%. The accuracy of the sequential extraction procedure was verified by comparison of the difference between the sum of each phase concentration and the total digested concentration. The recovery ((species sum/total As) × 100) was 86–104%, showing a satisfactory quality control.

### 2.4. Statistical analysis

The data statistical analysis was performed using statistical package, SPSS 11.0 for Windows (SPSS Inc., USA). Correlation analysis between rice arsenic concentrations and soil properties was performed using the Pearson correlation procedure. Statistical significance of differences was computed using one-way ANOVA.

## 3. Results and discussion

### 3.1. Soil properties and As speciation

The soil texture was assessed by field identification according to former Soviet Union standard. Most of the studied samples were light loam soils (63%), while the rest were medium loam (16%) and sandy loam soils (21%). The soils were slightly acid, with pH ranging from 4.4 to 7.4 (mean 5.7) (Table 1). The organic matter (OM) content of soil ranged from 4.6 to 89.5 g/kg with a mean value of 29.0 g/kg. Total soil P and Si varied widely, ranging from 206 to 1373 mg/kg and 62.1–462 g/kg, respectively, with the mean values of 493 mg/kg and 222 g/kg, respectively. The soil available P and Si varied from 10.8 to 37.6 mg/kg and 10.0–157 mg/kg, respectively, with the mean concentrations of 21.1 and 48.4 mg/kg, respectively.

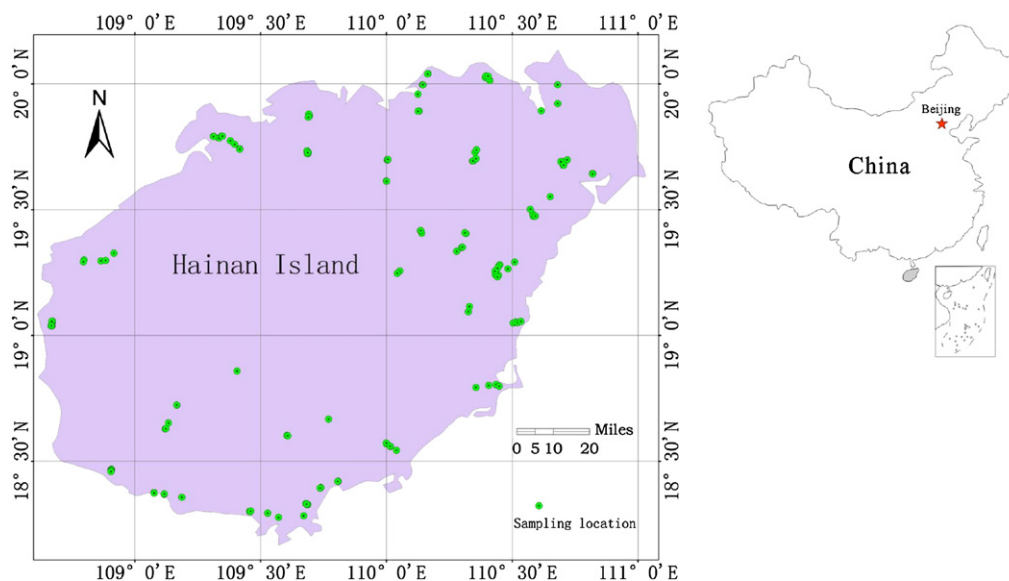


Fig. 1. Study area and sampling locations.

**Table 1**  
Properties of the paddy soils from Hainan Island.

	n	Mean	Median	Min	Max	S.D.
pH	141	5.7	5.6	4.4	7.4	0.6
OM (g/kg)	141	29.0	25.8	4.6	89.5	14.9
P (mg/kg)	141	493	422	206	1373	238
P <sub>available</sub> (mg/kg)	141	21.1	21.4	10.8	37.6	4.3
Si (g/kg)	141	222	182	62.1	462	124
Si <sub>available</sub> (mg/kg)	141	48.4	43.6	10.0	157	27.8
As <sub>total</sub> (mg/kg)	141	3.0	1.5	0.1	45.9	6.1

Total As concentrations were in the range of 0.1–45.9 mg/kg. The mean of 3.0 mg/kg was much lower than many published results for paddy soils (e.g. Huang et al., 2006; Lu et al., 2010). The lower concentrations of As were found on the acid igneous rocks and basalt, ranging from 0.1–5.9 mg/kg and 0.2–4.2 mg/kg, respectively, mean of 1.0 mg/kg and 1.4 mg/kg, respectively. Soils from clastic sediments had medium As values, ranging from 0.4–10.9 mg/kg, mean of 2.6 mg/kg. Higher levels were found in metamorphic rocks ranging from 18.9 to 45.9 mg/kg, with a mean of 35.4 mg/kg. These high concentrations might be attributed to the high As levels in phyllite (33–59 mg/kg, unpublished data) from these sampling area.

The potential mobility and toxicity of elements within soils depend on their chemical species rather than total concentrations. In this study, we adopted the Tessier's sequential extraction procedure to determine the speciations of As in the paddy soil. Although this method was designed originally for the extraction of cationic metals, many studies showed that it can also be used to predict the mobilization potential of oxyanions such as As (Voigt et al., 1996; Roussel et al., 2000; Li et al., 2009a; Batjargal et al., 2010). It should be noted that we modified the Tessier's procedure from five steps to six steps by adding a Humic acids (HA) bound fraction. This is due to the consideration that HA are highly active components of soil organic matter in binding metal ions, which may affect greatly the distribution and transport of As in soil (Wang and Mulligan, 2006, 2009; Newton et al., 2006). The extraction result is listed in Table 2. The residual As (mean 57.9%) was the dominant fraction in the Hainan paddy soil, followed by HA bound fraction (mean 21.7%) and Fe–Mn oxides bound fraction (13.8%). The ratios of OM and sulfides bound fraction (mean 4.1%), carbonate bound fraction (mean 2.0%), and exchangeable fraction (mean 0.1%) were relatively low. Residual and Fe–Mn oxides bound As had also been shown to dominate in other studies (Voigt et al., 1996; Okonkwo, 2007; Li et al., 2009a), revealing the immobile nature of As and its high affinity for adsorption by Fe–Mn (hydr) oxides in soil. Li et al. (2009a) in their study found that the residual As in paddy soil accounted for 90.15–96.37% of the total, while the

**Table 2**  
Arsenic speciation of the paddy soils from Hainan Island.

		Mean	Median	Min	Max	S.D.
F1	mg/kg	0.009	nd <sup>a</sup>	nd	0.37	0.05
	%	0.1	nd	nd	2.5	0.4
F2	mg/kg	0.054	0.014	nd	1.21	0.16
	%	2.0	0.99	nd	29.6	3.7
F3	mg/kg	0.53	0.27	0.006	6.32	0.86
	%	21.7	19.7	0.4	59.1	11.4
F4	mg/kg	0.33	0.19	nd	3.54	0.52
	%	13.8	13.9	nd	35.6	7.6
F5	mg/kg	0.088	0.029	0.003	1.72	0.24
	%	4.1	2.7	0.09	32.7	4.4
F6	mg/kg	1.84	0.75	0.041	30.38	4.19
	%	57.9	58.7	12.2	94.3	15.9

<sup>a</sup> nd: not detected.

ratios of the other fractions were generally lower than 5%. The comparatively lower ratio of residual As in our study was probably due to the relatively high pH and low clay content of the soil (Li et al., 2009a). However, HA bound As in this study was more important than the Fe–Mn oxides bound fraction in the paddy soil, probably indicating the more strong affinity of As binding to the HA or the inhibit effect of As adsorption by Fe–Mn oxides in the present of HA. HA is negatively charged and show a high affinity for adsorption to the metal (hydro) oxide surfaces. Therefore, they tend to compete with As(V) and As(III) anions for adsorption to the Fe–Mn oxide surfaces (Wang and Mulligan, 2006). Furthermore, it has been shown that HA could contribute more to the retention process in acidic environments than clays and some hydrous oxides (Thanabalasingam and Pickering, 1986). So, the slightly acid condition of the paddy soils would facilitate the adsorption of As by HA.

### 3.2. Arsenic in rice

Arsenic distribution in brown rice grain from Hainan was showed in Table 3. The As concentration in Hainan rice grain varied greatly, from 5 to 308 µg/kg and 6–281 µg/kg for early rice and late rice, respectively. The mean As for the whole samples was 92 µg/kg with no statistical difference between the early rice (92 µg/kg) and the late rice (91 µg/kg). This value was lower (or not higher) than results from most Chinese provinces/cities, except Xining (mean 54 µg/kg) and Hong Kong (mean 80 µg/kg) (Table 3). However, the range of As concentration in the present study was wider than most regions of China (Table 3), this is due to the contribution of three higher samples (275, 281, and 309 µg/kg, respectively). Zhu et al. (2008a) reported an average As concentration of Chinese rice to be 114 µg/kg, while it was 140 µg/kg in Meharg's study (Meharg et al., 2009). Arsenic concentration of our rice was 19–34% lower than these data. A comparison of our study with data published for other countries (Table 3) showed that As level in Hainan rice grain was lower than the results obtained from France (280 µg/kg), U.S. (250 µg/kg), Spain (200 µg/kg), Japan (190 µg/kg), Italy (150 µg/kg), Thailand (140 µg/kg), and Bangladesh (130 µg/kg), but still much higher than Egypt (50 µg/kg) and India (70 µg/kg). But, it should be noted that most data collected for comparison were from white (polished) rice (Table 3). The predicted As concentration (mean 48 µg/kg) in white rice (endosperm) of our study according to Williams et al. (2009) would be lower than all of the published data.

Recent researches have shown that brown rice has in fact higher levels of both total As and inorganic As (As<sub>i</sub>) than white (polished) rice, due to the localization of As<sub>i</sub> in the bran layer (Zavala and Duxbury, 2008; Zhu et al., 2008b; Meharg et al., 2008; Sun et al., 2008). Sun et al. (2008) reported that rice bran, both commercially purchased and specifically milled, have levels of As<sub>i</sub> reaching concentrations of 1000 µg/kg. Therefore, the people who take brown rice or rice bran products as "Health food" would considerably increase their As<sub>i</sub> exposure (Zhu et al., 2008b; Sun et al., 2008). However, our study showed that brown rice from Hainan contained much lower As concentration. In order to better understand the contaminated status, we compared our data with the maximum contaminant level (MCL) for As<sub>i</sub> in rice (150 µg/kg) according to the Chinese standard (CFSA, 2005). Result showed that most samples (84% for early rice and 90% for late rice) from Hainan contained total As concentrations lower than the MCL. In this study, the As<sub>i</sub> has not been separated. However, many studies found that As<sub>i</sub> in rice grain correlated strongly to total As concentration (Zhu et al., 2008a; Lu et al., 2010). If we calculated using a predicting model for grain As<sub>i</sub> described by Zhu et al. (2008a), the mean As<sub>i</sub> concentration would be 57 and 56 µg/kg for early rice and late rice, respectively, which was significantly lower than the mean level for

**Table 3**  
Arsenic concentration in rice grain from Hainan Island and other countries/regions.

Country	Province/city	n	Mean ( $\mu\text{g}/\text{kg}$ )	Median ( $\mu\text{g}/\text{kg}$ )	Min ( $\mu\text{g}/\text{kg}$ )	Max ( $\mu\text{g}/\text{kg}$ )	Reference
China	Hainan <sup>a</sup>	282	92	86	5	309	This study
	Early rice	141	92	82	5	309	
	Late rice	141	91	91	6	281	Zhu et al., 2008a
	Guangxi	39	155	127	41	586	
	Guangzhou	30	102	97	59	245	
	Hong Kong	19	80	83	15	138	
	Jiangxi	30	145	145	68	250	
	Shanghai	34	105	107	51	163	
	Jiangsu	25	88	85	29	137	
	Guizhou	31	90	92	19	162	
	Liaoning	5	108	89	68	162	
	Heilongjiang	11	124	109	73	187	
	Jilin	4	129	134	91	158	
	Hebei	2	128	128	98	158	
	Northeast unknown province	10	118	115	67	188	
	Fujian <sup>a</sup>	36	116.5		41.0	201.0	Huang et al., 2006
	Guangxi	45	230		111	372	Qin et al., 2006
Xining	37	54	52	14	97	Chang, 2010	
Bangladesh		144	130	130	20	330	Meharg et al., 2009
Egypt		110	50	40	10	580	
France		33	280	230	90	560	
India		133	70	70	10	180	
Italy		38	150	130	70	330	
Japan		26	190	180	70	420	
Spain		76	200	140	50	820	
Thailand		54	140	130	10	390	
U.S.		163	250	250	30	660	

<sup>a</sup> Brown (unpolished) rice.

Chinese rice (96  $\mu\text{g}/\text{kg}$ ) reported by Zhu et al. (2008a) and only 1% of the rice samples exceeded the MCL. This finding indicates that most brown rice grains from Hainan are safe for consumption. However, it should still take care if the rice bran is separated solely as health food materials.

### 3.3. Relationships between rice as and soil properties

For a single cultivar, the variation of As concentration in the rice grain mainly depended on environmental conditions, especially soil properties (Norton et al., 2009; Lu et al., 2009). In this study, we focus on the soil pH, OM, P, Si, and soil As speciation, since these parameters had been proved to be the most important factors in controlling the uptake of soil As by plants. The result of Pearson correlation analyses between grain As concentrations and these considered soil properties is listed in Table 4.

#### 3.3.1. pH and OM

The solubility and bioavailability of As in soil is affected by changes in pH. But there is not a universal agreement on this issue. In general there is an increase in arsenic mobility as the soils become more acid, particularly at pH values below 5 when arsenic-binding species such as Fe and Al oxy-compounds become more soluble (Carbonell-Barrachina et al., 1999). Signes-Pastor et al. (2007) reported that low pH values (<5.5) resulted in higher soluble concentrations of As in soil solution. However, the uptake of arsenic by plants may be increased on higher pH soil (Campbell et al., 1985). Pansar-Kallio and Manninen (1997) found that pH

changed in the environment would have to be very dramatic, i.e. pH 13, if they were to release high amounts of arsenic bound to the soil. In the present study, there was no obvious relationship between rice grain As concentration and the soil pH, indicating the less impact of these soil pH (4.4–7.4) on the accumulation of As in the rice grain. In fact, pH affects the As behavior generally by controlling the interaction between As and its bearing phases, instead of direct action.

Organic matter has great potential in influencing As sorption behavior by interacting with mineral surfaces and/or with As itself. The presence of nature organic matter may enhance As release mainly through competition for available adsorption sites, forming aqueous complexes, and changing the redox chemistry of site surfaces and As species (Wang and Mulligan, 2006). On the other hand, organic acids could also reduce As mobility by serving as a binding agent and/or by forming insoluble complexes, especially when saturated with metal cations (Wang and Mulligan, 2006; Das et al., 2008). The negative correlation between rice grain As concentration and soil OM suggested that OM present in the paddy soil might reduce As bioavailability for the rice plant.

#### 3.3.2. P and Si

Arsenite and arsenate behave as analogs of silicic acid and phosphate, respectively, in terms of plant transport. As<sub>3</sub> enters the roots either as arsenite taken up by rice roots through the highly efficient Si transport pathway, or as arsenate via arsenate/phosphate cotransporters (Norton et al., 2010, and references therein). Therefore, silicic acid and phosphate may compete with As for

**Table 4**  
Pearson correlation between rice grain As concentration and soil properties.

	pH	OM	P	P <sub>available</sub>	Si	Si <sub>available</sub>	Total As	F1	F2	F3	F4	F5	F6
Grain As (n = 141)	-0.045	-0.359***	-0.168*	-0.211*	-0.059	-0.142	0.260**	0.185	0.300**	0.395***	0.352***	0.172*	0.218**

\*Significant level at  $p < 0.05$ , \*\* $p < 0.01$ , \*\*\* $p < 0.001$  (two tailed).

uptake and result in a decrease of As concentration in the plant (Bogdan and Schenk, 2009; Norton et al., 2010). In this study, total soil P and available P correlated significantly to the grain As, while there was no correlation between soil Si and grain As, which indicated that soil P is more important than soil Si in decreasing grain As uptake. However, it has been reported that the application of Si fertilization decreased the total As concentration in rice straw and grain by 78 and 16%, respectively (Li et al., 2009b). Guo et al. (2007) found that the addition of Si to the growth medium significantly reduced rice shoot and root As concentrations. But this inhibitory effect is not mediated by direct competition between As and Si for uptake sites on root cell membranes, which differs from that of P. In the study of Norton et al. (2010), no correlation was observed between shoot Si and grain As thus they speculated that although the uptake of arsenite and methylated As into shoots is mediated by the Si uptake mechanisms, translocation of As from shoots to grain, especially the unloading of As into the grain, may involve other transporters (i.e. phosphate transporters). The similar result from our study supports this hypothesis.

### 3.3.3. As speciation

The significant correlation between soil As and grain As revealed the influence of soil As pools on the accumulation of As in the rice grain. Arsenic speciation obtained by sequential extraction procedure would provide detail information about this issue. Except

exchangeable As (F1), all of the other fractions (F2–F6) correlated significantly to the grain As, suggesting the potential bioavailability of these phases for uptake by rice plant. The lack of correlation between F1 and grain As was probably due to the low concentrations of F1 of the soil. Among the fractions of F2–F6, HA bound fraction (F3) and Fe–Mn oxides bound fraction (F4) correlated most closely to the grain As. Moreover, these two fractions were most abundant (except F6) in the soils. This suggested that F3 and F4 were the most important pools for the rice plant. When paddy soil flooding, the reducing condition and the subsequently dissolve of Fe–Mn (hydr)oxides would lead to the leaching of Fe–Mn (hydr)oxides bound As into the soil solution (Blodau et al., 2008). Furthermore, As can bind to the humic substances through metal-bridging mechanisms (Wang and Mulligan, 2006), hence the dissolve of the metals, especially Fe, under reducing condition may release As from the humic acids. It has been reported that As can be released by the reductive dissolution of FeOOH or MnOOH linked to humic substances (Selim Reza et al., 2010). So, the fractions of F3 and F4 in this study could be taken as predictors of As concentrations in the rice grain.

It has been showed that grain arsenic concentrations increased sharply at low soil concentrations and plateauing at higher concentrations (Adomako et al., 2009; Williams et al., 2007; Lu et al., 2009). Adomako et al. (2009) argued that as shoot As concentration increases, phototoxicity sets and certain cell metabolic activities are interfered with thus impeding As transfer to the grain. It is also possible that a physiological switch comes into play when shoot As content reaches a critical level. Lu et al. (2009) found that the overall soil–grain As relationship can be described by a hyperbolic model, with grain As levels start to plateau at soil concentrations above  $\sim 5$  mg/kg. The present study showed a similar but more detail result by the sequential extraction. We found that the soil–grain relationship might be best described by a periodically separate linear model (Fig. 2). The slopes between soil As speciation and grain were steep at total soil As concentration lower than 3.6 mg/kg and gentle at higher concentrations.

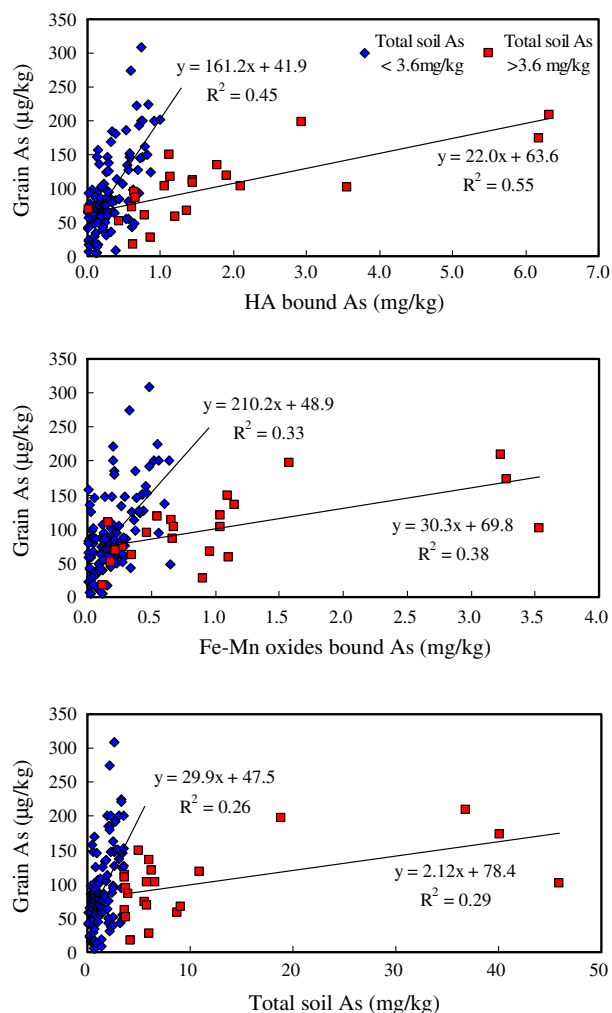


Fig. 2. Correlation of As concentration between rice grain and soil As speciations.

## 4. Conclusion

Arsenic concentration in the brown rice grain from Hainan Island, China was lower than most published data and the Chinese MCL, suggesting that they are safe for consumption. The factors influencing the uptake of As by rice grain in this study included soil As speciation, soil OM and P contents. Though its limitation, the sequential extraction procedure can provide useful information about As mobility/availability in the paddy soil, which showed that the humic acid bound and Fe–Mn oxides bound As in the paddy soils might be the most important pools for potential uptake by rice plant. This study also found that the transfer of soil As to the rice grain was steep at low soil As concentrations and gentle at higher concentrations.

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