



Cadmium availability in rice paddy fields from a mining area: The effects of soil properties highlighting iron fractions and pH value



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ABSTRACT

Cadmium (Cd) availability can be significantly affected by soil properties. The effect of pH value on Cd availability has been confirmed. Paddy soils in South China generally contain high contents of iron (Fe). Thus, it is hypothesized that Fe fractions, in addition to pH value, may play an important role in the Cd bioavailability in paddy soil and this requires further investigation. In this study, 73 paired soil and rice plant samples were collected from paddy fields those were contaminated by acid mine drainage containing Cd. The contents of Fe in the amorphous and DCB-extractable Fe oxides were significantly and negatively correlated with the Cd content in rice grain or straw (excluding DCB-extractable Fe vs Cd in straw). In addition, the concentration of HCl-extractable Fe(II) derived from Fe(III) reduction was positively correlated with the Cd content in rice grain or straw. These results suggest that soil Fe redox could affect the availability of Cd in rice plant. Contribution assessment of soil properties to Cd accumulation in rice grain based on random forest (RF) and stochastic gradient boosting (SGB) showed that pH value should be the most important factor and the content of Fe in the amorphous Fe oxides should be the second most important factor in affecting Cd content in rice grain. Overall, compared with the studies from temperate regions, such as Europe and northern China, Fe oxide exhibited its unique role in the bioavailability of Cd in the reddish paddy soil from our study area. The exploration of practical remediation strategies for Cd from the perspective of Fe oxide may be promising.

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1. Introduction

Cadmium (Cd) contamination in rice has attracted much attention in Asian countries because it poses a serious threat to human health. As previously reported, Cd intoxication can severely damage several human organs and systems, such as the respiratory system, kidneys, reproductive system and skeletal system (Godt et al., 2006). Rice is a staple food for most Asian populations, for which the dietary intake of rice is a major source of Cd to the human body (Tsukahara et al., 2003). Due to rapid urbanization, mining and metal processing, Cd pollution occurs widely in China, especially in paddy soil of South China (Wang et al., 2014b). In a previous study, Cd contents were reported to exceed the allowable Cd limit (0.2 mg kg⁻¹) specified by the Chinese food security

standards in more than 10% of rice grain samples across China (Zhen et al., 2008).

Previous studies, especially studies from temperate regions, such as Europe, have demonstrated that metal phytoavailability is affected by soil properties, such as the pH, organic matter (OM) content, clay content, cation exchange capacity (CEC) and available phosphorus (P) content (Brown et al., 2004; Romkens et al., 2011; Pietrzykowski et al., 2014). Of these properties, pH significantly influences metal phytoavailability. A recent study (Rafiq et al., 2014) indicated that the Cd contents in rice grains were significantly and negatively correlated with soil pH. In addition, several previous reports have established multiple regression models based on the correlation between pH and the crop uptake of Cd (McBride, 2002; Rafiq et al., 2014). Generally, the mobility and bioavailability of Cd increase as the soil pH decreases, because lower pH values enhance the transformation of Cd from an immobile form (e.g., carbonate and Fe and manganese (Mn) oxide bound forms) to an easily

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bioavailable form (e.g., the exchangeable form) (Xian and Shokohifard, 1989; Li et al., 2014a). Compared with studies from temperate regions, soils in (sub) tropical areas feature an abundance of iron (Fe) oxides with a higher redox activity, especially in paddy soil (Li et al., 2006). Thus, we hypothesized that the bioavailability of Cd in paddy soil from this region is closely related to the Fe oxide fractions in addition to other soil physicochemical properties. However, these factors require further investigation. In fact, the transformations of Fe-containing minerals can significantly affect the mobility of Cd in the soil and increase or decrease the bioavailability of Cd. For example, Fe oxides possess a significant capacity for Cd adsorption and can effectively immobilize Cd (Liu et al., 2014b). The secondary Fe minerals produced by Fe(III)-reducing bacteria and the bacteriogenic Fe oxides produced by Fe(II)-oxidizing microorganisms can all immobilize Cd (Martinez et al., 2004; Muehe et al., 2013). In addition, the Fe(II)-catalyzed recrystallization of Fe-(hydro)oxides can result in the incorporation of Cd (Cooper et al., 2006). Moreover, the reduction of Cd-bearing Fe(III) minerals by Fe(III)-reducing bacteria can directly enhance the mobility of Cd (Muehe et al., 2013). However, these studies were mainly based on laboratory experiments. Studies regarding the effects of Fe redox cycling on the mobility of Cd in paddy fields in the red soil region remain rare. Furthermore, the chemical fractions of heavy metals can influence the bioavailability and mobility of metals (Santos et al., 2002). Particularly, sequential extraction procedures can be used to investigate the geochemical partitioning of heavy metals among solid mineral and organic phases. The chemical forms of Cd are classified as exchangeable forms (bioavailable and mobile) and as carbonate, oxide, and organic forms (fixed and immobile) (Peijnenburg et al., 2007). Accordingly, examining the correlations between soil physicochemical properties, especially the Fe fractions and Cd fractionation in soils, can be useful for elucidating the mechanisms of Cd mobility and bioavailability.

The Lianhuashan tungsten mine, which is located in Shantou City and within Guangdong Province, is one of the largest tungsten mines in China. The paddy fields downstream of the mining area have received substantial influxes of mine drainage. In this study, 73 pairs of soil and rice plant samples were collected from rice paddy fields in the Lianhuashan tungsten mining area. A frequently used sequential extraction procedure was used to fractionate the soil Cd (Tessier et al., 1979). Additionally, the Cd contents were determined in different parts of rice plants. To identify the main factors affecting Cd availability in rice, especially the role of Fe redox cycling on Cd availability, this study aimed to assess the effects of Fe fractions and other soil physicochemical properties, such as pH, OM, soil P, and CEC, on the distributions of soil Cd and on the availability of Cd for rice plants under field conditions.

2. Materials and methods

2.1. Sampling

Soil and plant samples were collected from 73 different rice paddy fields downstream of the Lianhuashan tungsten mine in November 2010 (Fig. S1). The rice plants were separated into grain (brown rice), husk, straw, and root fractions. Rice straws and roots were washed with tap water and then rinsed with deionized water more than three times. After being dried, all plant materials were ground in a carnelian mortar before further chemical analysis. The soil samples were collected from the root zone of the rice samples, air-dried, and then crushed with a wooden hammer before passing through a 2 mm sieve for pH analysis and a 100-mesh sieve for Cd and the other physicochemical analyses. Further descriptions and details regarding the sampling information are provided in a

previous study (Liu et al., 2014a).

2.2. Physicochemical analyses

To measure the soil pH, 1 g of air-dried soil was extracted with 1 M CaCl₂ (pH = 6.0) and then determined using a pH meter. The soil CEC was calculated as the sum of Ca + Mg + K + Na extracted with 1 M NH₄-acetate. The OM content was determined using the potassium dichromate volumetric method. The available phosphorus and total phosphorus contents were measured using the Mo–Sb anti-spectrophotography method. The contents of soil Fe fractions including DCB-extractable Fe, amorphous Fe, HCl-extractable Fe(II) and Fe(III) have been reported in a previous study (Liu et al., 2014a). The detailed soil physicochemical analysis procedures were described previously (Lu, 2000).

2.3. Cd Content in the soils and rice plants

Approximately 0.5 g of each soil sample was digested in 5 mL of HNO₃ and HClO₄ (4:1, v:v) at 140–160 °C. In addition, approximately 1 g of each plant sample was digested in 1.0 mL of HClO₄, 1.5 mL of H₂SO₄ and 4.0 mL of HNO₃ at 110–130 °C until a clear solution was obtained. All of the digested samples were adjusted to a constant volume depending on the content of Cd in the samples with 2% HCl, passed through a 0.45 μm filter and then analyzed for the total Cd using a graphite furnace atomic absorption spectrometer (ZEEnit 60, Analytik Jena, Germany). All reagents were of analytical grade or better and obtained from Guangzhou Chemical Co., China. To verify the accuracy of the metal analysis, certified reference materials, obtained from the National Research Center for Standards in China were used (GBW 07429 for the soils and GBW 10023 for the plants). The certified Cd contents in the GBW 07429 and GBW 10023 reference materials were 0.21 ± 0.02 and 0.57 ± 0.05 mg kg⁻¹, respectively. The results of our study (n = 12) provided mean Cd contents of 0.20 ± 0.03 and 0.61 ± 0.03 mg kg⁻¹ for the GBW 07429 and GBW 10023 materials, which corresponded to 95% and 107% of the target values, respectively. Reagent blanks and analytical duplicates were used to ensure the accuracy and precision of the analysis.

2.4. Soil Cd fractionation

A sequential Cd fractionation scheme based on a previous method (Tessier et al., 1979) was used to determine the following operationally defined Cd fractions: F1, Exchangeable fraction, adding 20 ml 1.0 M MgCl₂ (pH = 7.0) to 1 g soil and shaking for 4 h, centrifugal separation at 3000 r/min for 15 min, collecting the supernatant and then adding 10 ml 1.0 M MgCl₂ (pH = 7.0) to the precipitate and mixing on a rotary shaker, centrifugal separation, collecting the supernatant, repeating this procedure for three times and combining all the supernatants, adjusting to 50 mL with water and measure using a graphite furnace atomic absorption spectrometer; F2, Bound to carbonate fraction, adding 10 ml 1 M NaOAc/HOAc (pH = 5.0) to the precipitate from F1 and shaking for 6 h, centrifugal separation at 3000 r/min for 15 min, collecting the supernatant and adding 10 ml 1 M NaOAc/HOAc (pH = 5.0) to the precipitate and mixing on a rotary shaker, centrifugal separation, collecting the supernatant, repeating this procedure for three times and combining all the supernatants, adjusting to 50 mL with water and measure using a graphite furnace atomic absorption spectrometer; F3, Fe and Mn oxide bound fraction, adding 20 ml 0.1 M NH₂OH–HCl to the precipitate from F2 and shaking for 6 h, centrifugal separation at 3000 r/min for 15 min, collecting the supernatant and adding 10 ml 0.1 M NH₂OH–HCl to the precipitate and mixing on a rotary shaker, centrifugal separation, collecting the

supernatant, repeating this procedure for three times and combining all the supernatants, adjusting to 50 mL with water and measure using a graphite furnace atomic absorption; F4, organic-bound fraction, adding 20 ml 30% H₂O₂ (adjusted to pH 2 with HNO₃) to the precipitate from F3, shaking under 85 °C until nearly dry and adding 5 ml 30% H₂O₂ after cooling, shaking under 85 °C until nearly dry and adding 5 ml 3.2 M NH₄Ac, stirring for 30 min, centrifugal separation, adjusting the supernatant to 50 mL with water and measure using a graphite furnace atomic absorption spectrometer; F5, the residual phase, collecting the precipitate from F4, drying and extraction with 10 ml HCl–HNO₃–HClO₄, then measuring the supernatant using a graphite furnace atomic absorption spectrometer. The accuracy of the sequential extraction procedure was verified by comparing the differences between the sum of the Cd content in each phase and the total Cd content. The recovery ((fractions sum/total Cd) × 100%) was 89–107%, which indicates satisfactory quality control.

2.5. Statistical analyses

Statistical analyses of the experimental data were performed using the SPSS[®] 10.0 (SPSS, USA) software. The correlation analysis was conducted using a Pearson's correlation test with a significance level of $P < 0.05$ (two-tailed). In addition, random forest (RF), one of the most accurate learning algorithms, was used to evaluate the factors affecting Cd bioavailability in rice (Breiman, 2001a, 2001b). Stochastic gradient boosting (SGB), one of the most powerful methods for predictive data mining in recent years (Friedman, 2001; Wang et al., 2015) was also used to compare with the results from RF. For our datasets, the Cd content of the rice grain was used as the dependent variable and all of the other parameters were used as independent variables (including contents of Fe in the amorphous and DCB-extractable Fe oxides, Cd content in straw, concentrations of HCl-extractable Fe(II) and Fe(III), contents of Cd in F1, F2, F3, F4 and F5, total soil Cd content, Cd content in root, OM content, total soil P content, available soil P content, CEC, pH, total soil Fe content and root Fe content).

3. Results and discussion

3.1. Accumulation and distribution of Cd in rice plants

The total Cd contents in the rice grains, straws and roots of rice plants ranged from 0.04 to 0.33, 0.08 to 3.6 and 1.0 to 11 mg kg⁻¹, respectively, with mean ± SD values of 0.15 ± 0.06, 1.5 ± 0.90 and 5.4 ± 2.9 mg kg⁻¹, respectively (Table 1). The Cd content in 20% of the rice grain samples exceeded the allowable limit (0.2 mg kg⁻¹) that was specified by the Chinese food security standards. Regarding the different tissues of the rice plants, the Cd content decreased in the following order: root > straw > rice grain. Thus, the accumulation of Cd was highest in the rice roots among the three investigated rice plant tissues. In particular, the Cd contents in the roots were approximately 2 and 12 times the contents in the straw and rice grain, respectively. Similar results were also obtained in a previous study (Yang et al., 2006), which indicated that Cd mainly accumulated in the rice roots. Furthermore, the Cd contents in the rice roots and straw or rice grain were significantly and negatively correlated with each other ($r = -0.592$ and $p < 0.01$ or $r = -0.407$ and $p < 0.01$; Fig. 1). These results indicated that the accumulation of Cd in the rice roots may reduce the amount of Cd that was translocated to the plant tissues above the ground (Liu et al., 2004; Rahman et al., 2007).

3.2. Fractionation of Cd in the soil and its implications for Cd bioavailability in rice

The total Cd contents in the 73 paddy soil samples ranged from 0.22 to 1.6 mg kg⁻¹ with a mean value of 0.66 mg kg⁻¹ (Table 1). Of these soil samples, 93% contained Cd contents above the allowable limit (0.3 mg kg⁻¹) specified by the Chinese soil environmental quality standards for farmland. The contents of Cd in the F1, F2, F3, F4 and F5 fractions accounted for 6.7%, 10.2%, 18.3%, 25.4% and 39.5% of the total Cd content, respectively. These results indicated that the residual and Fe–Mn oxides fraction contained most of the Cd in the paddy soil. The contents of Cd in F1 and F2 were significantly and positively correlated with the Cd contents in the rice grain or straw (Fig. 2). By contrast, no significant correlation was observed between the Cd in the rice grain or straw and the Cd in the other fractions (Table S1). Generally, the metals in the exchangeable fraction (F1) are considered more labile and more bioavailable. However, the bioavailability of the metals in the carbonate-bound fraction (F2) remains controversial (Fan et al., 2014). The results of our study indicated that the Cd fractions in F1 and F2 were highly available to rice. Regarding the availability of the Fe–Mn oxide-bound fraction (F3), previous studies (Fan et al., 2002; Baumann and Fisher, 2011) have indicated that this fraction is negatively correlated with the metal assimilation efficiency (AE) (AE = (Ingestion – Excretion – Egestion)/Ingestion) by worms, which indicates a low bioavailability.

3.3. Correlations between the Fe fractions in the soil and Cd fractions or the bioavailability of Cd in rice

The mean Cd content in the soils of our study was greater than those from the Yellow River Delta in North China (16.8 and 29.3 g kg⁻¹) and in France (14.5 g kg⁻¹) (Pauget et al., 2012; Li et al., 2014b). Detailed data for the different Fe fractions in the soil are provided in a previous study (Liu et al., 2014a). The contents of Fe in the amorphous Fe oxides were significantly and negatively correlated with the contents of Cd in F1 and F2 (Fig. 3). This result suggests that increasing the content of Fe in the amorphous Fe oxides could reduce the Cd fractions in F1 and F2. By contrast, the concentration of HCl-extractable Fe(II) was significantly and positively correlated with the contents of Cd in F1 ($r = 0.236$, $p < 0.05$) and F2 ($r = 0.283$, $p < 0.05$) (Fig. 3). Thus, enhancing the reduction of Fe(III) could increase the Cd contents in F1 and F2. Therefore, we concluded that the Fe fractions probably affected the proportional distribution of Cd in the soils and the Cd mobility. Furthermore, the contents of Fe in the amorphous and DCB-extractable Fe oxides were significantly and negatively correlated with the Cd content in rice grain or straw (excluding DCB-extractable Fe vs Cd in straw) (Fig. 4). These results again indicate that Fe fractions may play an important role in decreasing the Cd bioavailability in rice. However, no significant correlation between the content of Fe in the amorphous Fe oxides and the Cd content in F3 (Fe and Mn oxide bound fraction) was found in our study. Hence, regarding for the effect of Fe oxides on Cd availability, there may be some other mechanisms which we have not known. Many previous studies have suggested that intense Fe redox reactions in the rhizosphere of rice plants could strongly affect Cd bioavailability (Zhang et al., 2012). The oxygen transported from the aerial parts to the roots by the aerenchyma of rice plants enables the oxidation of ferrous iron to ferric iron, which deposits on root surface to form an iron plaque (Hu et al., 2015). The previous results obtained indicated that the Fe plaque may have positive, negligible, or no effects on Cd uptake and several possible mechanisms have been proposed (Zhang et al., 2012). Based on the results of our study, we speculated that the accumulation of Cd in rice roots should be attributed to the

Table 1

The soil properties, the Cd contents in the rice grains, straws and roots from 73 rice plants and the Cd fractions in 73 soil samples that were collected from the Lianhuashan mining area.

	Mean	Median	Standard deviation	Minimum	Maximum
OM ^a (%)	2.6	2.6	0.67	0.92	3.9
CEC ^b (cmol(+) kg ⁻¹)	10	11	3.6	4.9	19
pH	6.0	6.1	0.81	4.1	7.5
Fe ₀ ^c (g kg ⁻¹)	5.1	5.4	2.1	0.45	8.5
Fe _D ^d (g kg ⁻¹)	13	12	5.8	2.0	33
Fe(II) ^e (g kg ⁻¹)	0.14	0.14	0.04	0.06	0.27
Fe(III) ^f (g kg ⁻¹)	2.6	2.6	0.53	1.2	3.9
Available P ^g (mg kg ⁻¹)	88	90	42	3.2	187
Fe _T ^h (g kg ⁻¹)	42	41	16	11	83
F1 ⁱ (mg kg ⁻¹)	0.04	0.05	0.03	0.01	0.11
F2 ^j (mg kg ⁻¹)	0.07	0.06	0.03	0.02	0.15
F3 ^k (mg kg ⁻¹)	0.12	0.12	0.04	0.03	0.20
F4 ^l (mg kg ⁻¹)	0.17	0.17	0.10	0.01	0.47
F5 ^m (mg kg ⁻¹)	0.26	0.19	0.23	0.02	1.1
Cd _T ⁿ (mg kg ⁻¹)	0.66	0.61	0.30	0.22	1.6
Rice grain (mg kg ⁻¹)	0.15	0.14	0.06	0.04	0.33
Straw (mg kg ⁻¹)	1.5	1.6	0.90	0.08	3.6
Root (mg kg ⁻¹)	5.4	4.6	2.9	1.0	11

^a Organic matter.

^b Cation exchange capacity.

^c Amorphous iron (Fe), extracted with 0.2 mol L⁻¹ ammonium oxalate (pH 3.0).

^d DCB-extractable Fe, extracted with dithionite–citrate–bicarbonate (DCB).

^e Extracted with 0.5 mol L⁻¹ HCl.

^f Extracted with 0.5 mol L⁻¹ HCl.

^g Soil available phosphorus.

^h Total soil Fe.

ⁱ Cd Content in the soil extracted with 1 M MgCl₂ (Exchangeable fraction).

^j Cd Content in the soil extracted with 1 M NaOAc/HOAc (Bound to the carbonate fraction).

^k Cd Content in the soil extracted with 0.1 M NH₂OH–HCl (Fe and manganese oxide bound fraction).

^l Cd Content in the soil extracted with 30% H₂O₂ (adjusted to pH 2 with HNO₃) + 3.2 M NH₄Ac (organic-bound metal).

^m Cd Content in the soil extracted with HCl–HNO₃–HClO₄ (Residual phase).

ⁿ Total Content of the Cd fractions in the soil.

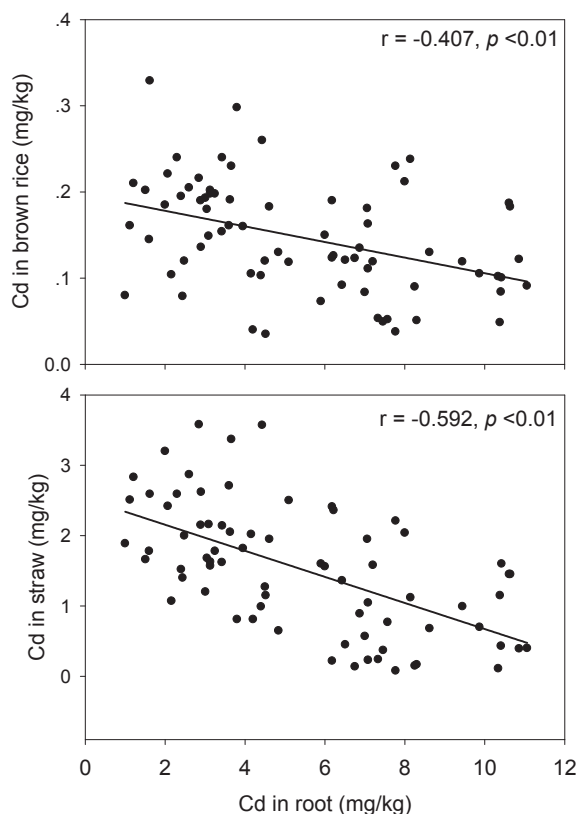


Fig. 1. Linear correlation analysis between the cadmium (Cd) contents in the rice roots, rice grains and rice straws.

sequestration of Fe plaque, which could be a mechanism for heavy metal detoxification in plants. Nevertheless, some questions remain unresolved related to the effect of Fe plaque on Cd uptake by rice due to the complexity of the issue and further works are needed in the future. In addition, the concentration of HCl-extractable Fe(II) was positively correlated with the Cd content in rice grain or straw (Fig. 4), which indicated that the HCl-extractable Fe(II) could be used as another indicator of Cd availability. The HCl-extractable Fe(II) could be derived from the reduction dissolution of the amorphous Fe oxides. However, it is noteworthy that the concentration of HCl-extractable Fe(II) accounted for only 5% of the content of Fe in the amorphous Fe oxides in our study. Therefore, the release of Cd to soil solution as a result of the reduction dissolution of amorphous Fe oxides was not the predominant process in our study.

3.4. The effect of other soil properties on the availability of Cd

The results from RF and SGB showed that the pH, F1, Cd content in straw, Cd content in root, F2, total soil Cd content and the amorphous Fe oxides content were the greatest contributors to Cd loading in the rice grains, with corresponding importance scores of 16.5%, 15.2%, 12.0%, 7.2%, 6.5%, 6.0% and 4.5% for RF and 22.5%, 14.6%, 12.7%, 7.6%, 4.5%, 5.4% and 4.2% for SGB, respectively (Fig. S7). Besides, in order to accurately assess the contribution of different environmental factors, the Cd contents in root and straw were excluded from RF and SGB analyses and the results are shown in Fig. 5. Of these factors, pH is the most important factor that affects Cd bioavailability, which was also observed in previous studies (Liang et al., 2013; Wang et al., 2014a). The pH values in all of the soil samples varied from 4.1 to 7.5 with a mean value of 6.0. Of these

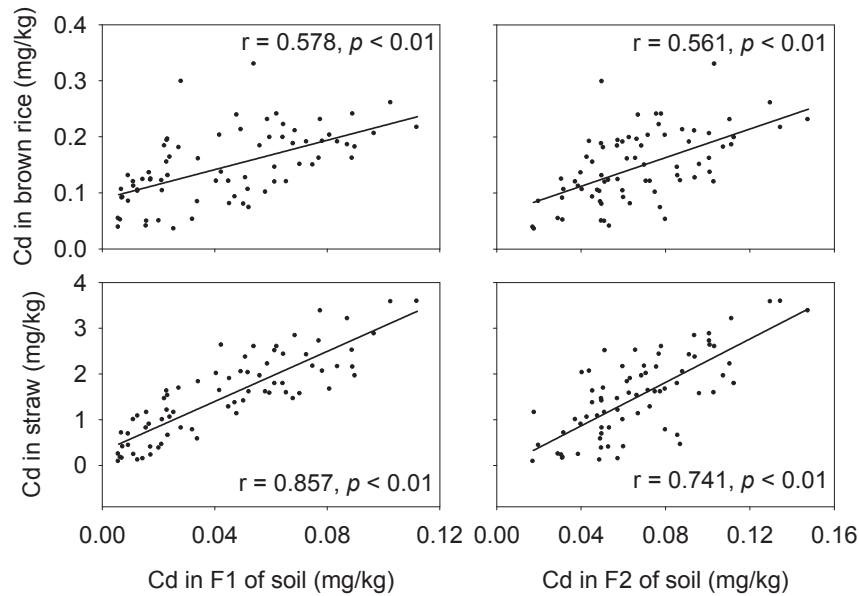


Fig. 2. Linear correlation analysis between the cadmium (Cd) contents in the rice (rice grain and straw) and Cd fractions (F1 and F2) in the soil. F1: extracted with 1 M MgCl₂ (Exchangeable fraction); F2: extracted with 1 M NaOAc/HOAc (Bound to carbonate fraction).

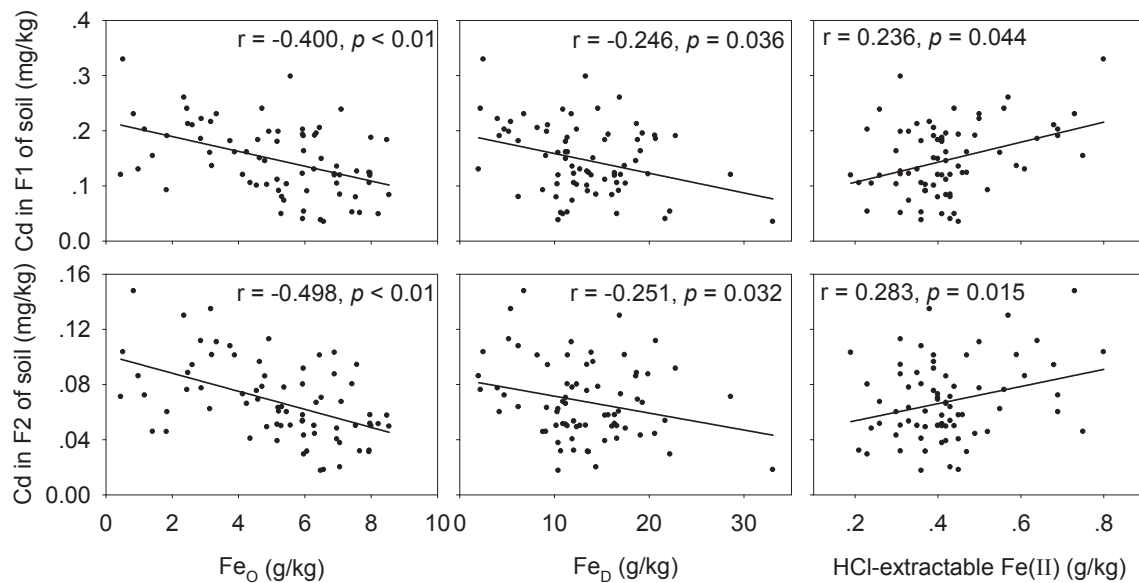


Fig. 3. Linear correlation analysis between the iron (Fe) fractions (Fe_O, Fe_D and Fe(II)) and the Cd fractions (F1 and F2) in the soil. Fe_O: extracted with 0.2 mol L⁻¹ ammonium oxalate (pH 3.0); Fe_D: extracted with dithionite–citrate–bicarbonate (DCB); Fe(II): extracted with 0.5 mol L⁻¹ HCl; F1: extracted with 1 M MgCl₂ (Exchangeable fraction); F2: extracted with 1 M NaOAc/HOAc (Bound to carbonate fraction).

soil samples, 2.7% had a pH of less than 4.5 (strongly acidic), 26% had a pH of 4.5–5.5 (acidic) and 33% had a pH of 5.5–6.5 (weakly acidic). Thus, the soil in the sampling region of our study has the typical red soil characteristic of low pH. Significant negative correlations were found between pH and the contents of Cd in F1 or F2 (Table S1), indicating that pH change could significantly affect the fractionation of Cd in the soils of our study. Generally, the concentration of dissolved Cd in the soil water increased as the soil pH decreased. Results from a previous study indicated that the effects of pH on the amount of Cd absorbed by a plant depends on its tolerance to low pH (Hattori et al., 2006). Because low pH conditions can inhibit plant growth and decrease Cd absorption. For example, substantial reductions in the growth of tops and roots

were observed at pH of 3.5 and 8.5 for rice plants and optimum pH for rice growth was 5.5 (Alam, 1981). Furthermore, a significant correlation occurred between the pH and the content of Fe in the amorphous Fe oxides ($r = 0.274, p < 0.05$, Table S1), which indicated that pH change could affect the content of Fe fractions. This finding is consistent with a previous report that pH can significantly affect the transformation of Fe oxides in soils (Li et al., 2006). Regarding the parameters related to soil properties, the content of Fe in the amorphous Fe oxide is another important factor that affects Cd bioavailability, which is demonstrated by our results in the preceding section. Moreover, previous studies have reported that nutrient elements such as P can affect Cd bioavailability (Chen et al., 2013). The available P content in the investigated soil ranged from

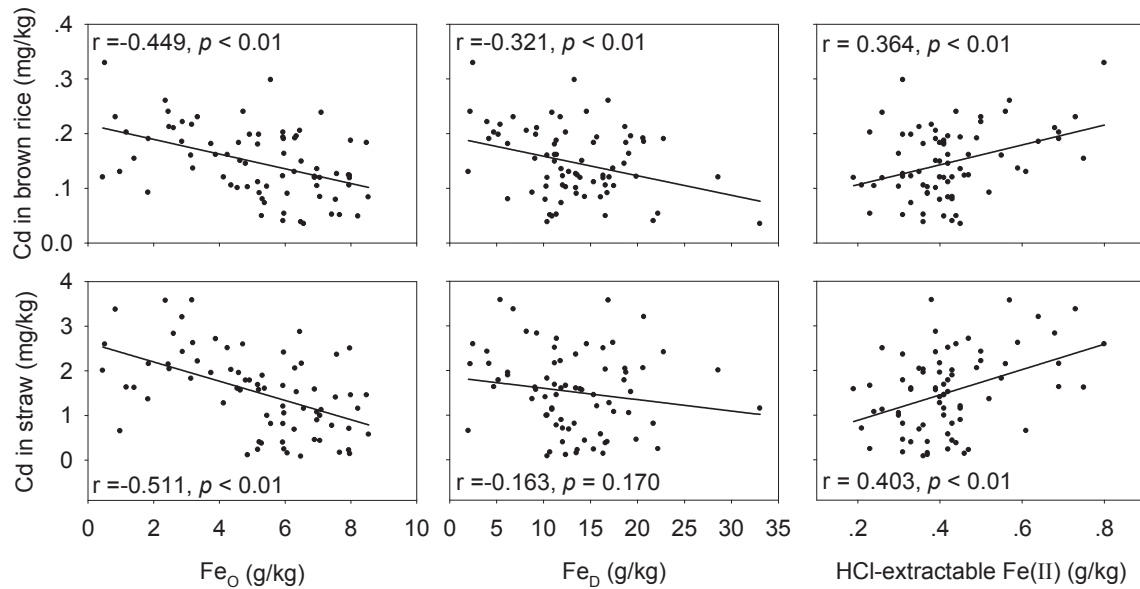


Fig. 4. Linear correlation analysis between the cadmium (Cd) content in the rice (rice grain and straw) and the iron (Fe) fractions (Fe_O, Fe_D and Fe(II)) in the soil. Fe_O: extracted with 0.2 mol L⁻¹ ammonium oxalate (pH 3.0); Fe_D: extracted with dithionite–citrate–bicarbonate (DCB); Fe(II): extracted with 0.5 mol L⁻¹ HCl.

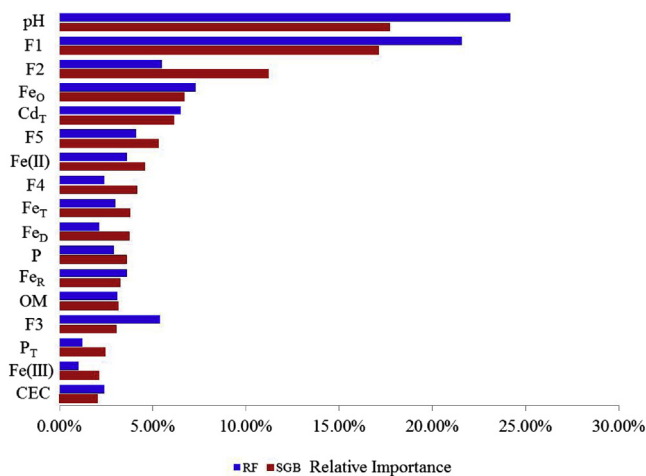


Fig. 5. Variable importance scores of the individual predictors (excluding Cd content in the straw and Cd content in the root) for estimating the Cd accumulation in rice grains based on random forest (RF) and stochastic gradient boosting (SGB) analyses. The importance values of the independent variables were rescaled by setting their sum to 100%. Fe_O: extracted with 0.2 mol L⁻¹ ammonium oxalate (pH 3.0); Fe_D: extracted with dithionite–citrate–bicarbonate (DCB); Fe(II): extracted with 0.5 mol L⁻¹ HCl; Fe(III): extracted with 0.5 mol L⁻¹ HCl; Fe_T: total Fe in the soil; Fe_R: Fe in the rice plant root; F1: Cd content in the soil extracted with 1 M MgCl₂ (Exchangeable fraction); F2: Cd content in the soil extracted with 1 M NaOAc/HOAc (Bound to the carbonate fraction); F3: Cd content in the soil extracted with 0.1 M NH₂OH–HCl (Iron and manganese oxide bound fraction); F4: Cd content in the soil extracted with 30% H₂O₂ (adjusted to pH 2 with HNO₃) + 3.2 M NH₄Ac (organic-bound metal); F5: Cd content in the soil extracted with HCl–HNO₃–HClO₄ (Residual phase); Cd_T: content of the total Cd fractions in the soil; OM: organic matter content; P_T: total soil phosphorus content; P: available soil phosphorus concentration; CEC: cation exchange capacity.

3.2 to 187 mg/kg, which is generally within the similar range of those (1.1–166 mg/kg) from Beibu Gulf economic zone (Jiang et al., 2014) but higher than those (5.6–19.9 mg/kg) from Taihu lake regions (Chen et al., 2012). As was reported, the total soil Cd content can increase due to the addition of P fertilizer (Jiao et al., 2012). Furthermore, the P content can influence the soil Cd fractionation (Zwonitzer et al., 2003). In some countries, such as Australia and

New Zealand, P fertilizers are considered to be major sources of heavy metal input in soils, especially for Cd (Bolan et al., 2003). The application of P compounds to soils may have no effect, may induce mobilization or may enhance the immobilization of metals. The exhibited effect depends on the nature of the P compound, the soil type, and the metal species (Bolan et al., 2003). In our study, the contribution of P to the decrease of Cd content in rice grain was 3.6% for RF and 2.9% for SGB, respectively (Fig. 5). Moreover, a significant negative correlation between the content of Cd in F1 and the available P content was observed ($r = -0.361$, $p < 0.01$, Table S1). However, no significant correlation occurred between the other Cd fractions and the available P content. Organic matter is an important soil component that can significantly affect the environmental behavior of Cd. For example, the bioavailability of heavy metals could be decreased through adsorption or through the formation of stable complexes with humic substances (Zeng et al., 2011). In addition, OM can supply organic chemicals such as humic acid and fulvic acid to the soil solution. These organic chemicals serve as chelates of metals and increase the bioavailability of metals in plants (Zeng et al., 2011). In this study, the soil OM content varied from 0.92% to 3.9% with a mean content of 2.6%. Furthermore, the OM contents in 43 soil samples were between 2.0% and 3.0% and were greater than 3.0% in 19 soil samples. However, in contrast with previous researches (Farrag et al., 2012; Waterlot et al., 2013) in which a significant correlation was observed between OM contents and metal availability, the contribution of soil OM to the bioavailability of Cd in rice was small in our study (Fig. 5), and no significant correlation was found between the soil OM contents and the Cd contents in the rice plants (Table S1). This difference is potentially related to the low soil OM content observed in our study relative to previous studies. The soil CEC provides a measure of the available sorption sites, so soils with greater CECs are very capable of sequestering metals (Janssen et al., 1997; Stewart et al., 2003). No significant correlation was observed between the Cd in the rice grain and the soil CEC (Table S1) and the contribution of CEC to Cd content in rice grain was very low (Fig. 5). By contrast, in the study conducted in northern China (Wang et al., 2004), the CEC was significantly correlated with the phytoavailability of metals. This difference may be resulted from the relatively low soil CEC in our

study area. Overall, compared with studies from temperate regions, such as Europe (Farrag et al., 2012; Waterlot et al., 2013) and northern China (Wang et al., 2004), the bioavailability of Cd in the reddish paddy soil from our study area exhibited unique characteristics. The pH and Fe fractions were more important than the other soil properties, such as the OM content, CEC and available P content.

3.5. Implication for the safety of paddy rice in South China

Cd content in rice grains can be significantly affected by soil properties. Firstly, the Cd contents in rice grains in the acid soil areas were significantly greater than those in the neutral soil areas (Zhang et al., 2009). This result demonstrated that low pH values in the acid paddy soils of South China resulted in greater Cd bioavailability. The pH value should be the most important factor in affecting Cd availability in paddy soil. Secondly, Fe fractions were significantly correlated with the bioavailability of Cd in rice grains. Thirdly, Fe plaque can sequester Cd and reduce its translocation to rice grains. The paddy fields examined in our study are located in South China and are characterized by reddish paddy soils containing abundant Fe oxides, which exhibit high reactivity and play an important role in environmental biogeochemistry (Li et al., 2006; Borch et al., 2010). The Fe redox cycling in paddy soil is more active compared to the other agricultural soils due to the alternate wetting and drying cycles that dramatically change the soil redox state. In addition, Fe redox cycling can be coupled with many environmental processes such as (im) mobilization of heavy metal, degradation of organic compounds and methane emission (Jackel et al., 2005; Kappler and Straub, 2005). However, to our knowledge, studies regarding the effects of Fe redox cycling on the fate of Cd in South China under actual field conditions are rare. Moreover, detailed mechanisms of Fe redox cycling on the bioavailability of Cd remain unclear (Zhang et al., 2012). Accordingly, additional studies that couple Fe redox cycling with the fate of Cd are needed. The results from our study indicate that the health threat derived from Cd exposure for people via the uptake of rice contaminated by Cd-containing acid mining drainage might be mitigated by regulating the soil pH and Fe fraction. Although some methods for reducing Cd concentrations in rice have been proposed (Lu et al., 2014; Singh and Prasad, 2014), the exploration of practical remediation strategies for Cd from the perspective of Fe redox cycling may be more economical and less disruptive.

Author contributions

Huan-Yun Yu and Chuanping Liu contributed equally to this work.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2015.11.021>.

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