



# Cadmium bioavailability well assessed by DGT and factors influencing cadmium accumulation in rice grains from paddy soils of three parent materials

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## Abstract

**Purpose** High Cd resulted from natural background or agricultural activities in some of the paddy soils in South China is a concern. It is imperative to understand the relationship between Cd bioavailability in high Cd soils and Cd accumulation in rice grains. Therefore, our objectives are to explore the relationship between Cd accumulation in rice grains and Cd availability which was characterized with five different methods, and to investigate factors influencing Cd accumulation in rice.

**Materials and methods** One hundred and twenty-two paired soil and rice plant samples were collected from paddy fields of three parent materials (sandshale, limestone, and Quaternary red earth) in Guangxi Province. Soil Cd availability was assessed using three chemical extractants (0.43 M HNO<sub>3</sub>, 0.01 M CaCl<sub>2</sub>, and 0.005 M DTPA) and compared with Cd in soil solution and that sampled by the diffusive gradients in thin films (DGT) method. A five-step sequential fractionation of Cd was also carried out. Random forest (RF) was employed for assessing factor relative importance in Cd accumulation in rice plants and grains in high Cd soils.

**Results and discussion** All of the soil samples had a total Cd content exceeding the maximum permissible concentration (0.3 mg kg<sup>-1</sup>) for soils with the exchangeable fraction taking up 50, 56, and 39%, respectively. For the rice grains harvested from the soils derived from sandshale, limestone, and Quaternary red earth, 67, 95, and 28%, respectively, had a Cd content exceeding the maximum permissible concentration for grain (0.2 mg kg<sup>-1</sup>). The results demonstrated high Cd bioavailability in these areas and indicated potential health risk when people ingest the rice grains. Cd measured by DGT best reflected Cd bioavailability. The Cd in soil solution (Cd<sub>soiln</sub>), which is directly available, and CaCl<sub>2</sub>-extracted Cd were also significantly related to grain Cd content. Factor relative importance assessment based on random forest (RF) showed that soil pH was among the top two most important physicochemical factors of the three types of soils influencing Cd accumulation in rice grains. Besides, dissolved organic carbon (DOC), clay, and dithionite-citrate-bicarbonate-extracted Mn (Mn<sub>DCB</sub>) was the other major influencing factor in the sandshale soils, limestone soils, and Quaternary red earths, respectively.

**Conclusions** The results indicated that DGT technique better predicted Cd bioavailability. Manipulating soil pH could be used to reduce Cd bioavailability and its accumulation in plants. However, manipulating soil DOC, clay and Fe/Mn content were soil-type-dependent.

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## 1 Introduction

Cadmium (Cd) is a toxic heavy metal. Soil Cd contamination caused by mining and industrial activities has been a great concern in China with “cancer village” and “toxic rice” occurring. Usually, the natural background content of Cd in the geosphere is small. However, there are places where Cd content is high in soil parent material, resulting in high soil Cd content. Worldwide, natural Cd background is reported to range between 0.02 and 6.2 mg kg<sup>-1</sup> (Adriano 2001). Natural Cd content in the top soil layer is higher in Guizhou and Guangxi Provinces in Southwest China than in the other regions of China (Ministry of Environmental Protection of China 1990). Natural Cd content in the surface soils (0–20 cm) ranges from 0.001 to approximately 13.430 mg kg<sup>-1</sup> in Guangxi Provinces, which is 1.75 times on average higher than that in the other regions of China (Ministry of Environmental Protection of China 1990). In Guangxi Province, the highest natural background content of Cd is in limestone soils (Zheng 1993). However, for paddy soils, agricultural activities such as fertilization and pesticide application could also be a source of Cd input during farming (Nookabkaew et al. 2016).

Rice (*Oryza sativa* L.) is a staple food in China especially in South China and easily uptakes Cd (Tsukahara et al. 2003). Thus, dietary intake of rice grown in soils with high Cd content could be a serious threat to human health due to itai-itai disease, cancer, cardiac failure, osteoporosis, and other diseases caused by Cd (Sebastian and Prasad 2014).

The available rather than total Cd determines the mobility and toxicity of Cd (Vig et al. 2003). Generally, Cd in soil solution or Cd extracted by traditional chemical extractants (e.g., dilute nitric acid, calcium chloride, low-molecular-weight organic acids, and diethylenetriaminepentaacetic acid) was considered as the directly or potentially available Cd pools in soils (Zhang et al. 2016). However, the accuracy of the results depends on the physicochemical characteristics of the soil, such as pH, redox conditions (Eh), soil organic matter (SOM), clay and cation exchange capacity (CEC), etc. Diffusive gradients in thin film (DGT), which was first proposed by Davison and Zhang (1994), is a passive sampling technology based on Fick's first law of diffusion. Consisting of a gel membrane and a resin, a DGT device functions similar to a plant root (Zhang et al. 2014). When deployed in the environment, the labile forms of metals diffuse through the gel membrane and are then adsorbed on the resin. Therefore, a DGT device can be used for in situ measurement and produces time averaged concentrations with high spatial resolution (Zhang et al. 2014). It has been proved that DGT is a technique that can well predict in situ metal bioavailability in such dynamic environments as waters, soils,

and sediments (Zhang and Davison 1995; Davison and Zhang 2012; Zhang et al. 2017a).

The availability of Cd is associated with soil properties such as clay, CEC, pH, SOM, dissolved organic carbon (DOC), Fe/Mn oxides, etc. (Zeng et al. 2011; Muehe et al. 2013a; Liu et al. 2017; He et al. 2017). For example, Rafiq et al. (2014) documented that Cd accumulation in rice grain negatively correlated with soil pH. He et al. (2017) reported that dissolved organic matter composition influenced the activities of Cd in sandshale-derived soil. Chen et al. (2000) noted that Cd activity was associated with the carbonates in soil (He et al. 2017). Readily adsorbed by Mn(III/IV)- and Fe(III)-(hydr)oxides, Cd is reduced in availability in soils such as Quaternary red earth which is high in Mn and Fe (Muehe et al. 2013a; Muehe et al. 2013b; Suda and Makino 2016; Yu et al. 2016).

As abovementioned, Cd availability is associated with soil properties which largely depend on soil types. In this study, three types of paddy soils in Guangxi Province were collected from places with high Cd concentration but no mining or industrial pollution sources nearby. Soil Cd extracted by three chemical extractants (0.43 M HNO<sub>3</sub>, 0.01 M CaCl<sub>2</sub>, and 0.005 M DTPA), Cd measured by the DGT method and Cd in soil solution were compared. Our objectives are (1) to explore the relationship between Cd accumulation in rice plants and Cd availability characterized with the five different methods and (2) to investigate factor relative importance in influencing Cd accumulation in rice plants for the soils.

## 2 Materials and methods

### 2.1 Sampling and sample pretreatment

One hundred and twenty-two paired soil and plant samples were collected from Xijiang River Basin in October 2015. The collected soil samples were derived from three different parent materials (limestone, sandshale, and Quaternary red earth). The sampling sites (with 42 paired soil and plant samples) of the sandshale-derived soils were located in Lingxiao Village, Liuxu Town, Jinchengjiang Area, and Hechi City. The limestone soil samples and the corresponding rice samples were collected from two sites in Jinchengjiang area of Hechi City: Jialiao Village, Dongjiang Town (25 paired) and Balun Village, Liuxu Town (15 paired). The Quaternary red earth-derived soil samples and corresponding plant samples (40 paired) were collected from Pinglu Village, Shuangqiao Town, Wuming Area, and Nanning City. There were no industrial or mining pollution sources around the sampling sites. The soils were air dried and grounded to < 2-mm sieve and <

0.15 mm for later analyses. The plant samples were separated into roots, straws, and grains, washed with tap water and deionized water, oven dried at 105 °C for 30 min, and followed by 70 °C until constant weight. Rice grain husks were removed using a dehulling machine (FC-2K, OTAKE, Japan). Plant samples were ground with an electric grinder (SL-100, China) for Cd analysis.

## 2.2 Soil physicochemical analyses

Soil pH was measured in a suspension of 1:2.5 (w/v) soil/water using a pH detector (PHS-2F, Leici, China). CEC was determined according to the method of Tan et al. (2017). SOM determination was performed using the potassium dichromate volumetric method. DOC (soil/water ratio of 1:5) was measured with a TOC analyzer (Elementar vario TOC, Germany). Particle-size analysis was analyzed using the sedimentation and pipette method (Zhang et al. 2017b). Free Fe/Mn oxides and amorphous Fe/Mn oxides contents were determined using atomic absorption spectrometry (AAS) following DCB and ammonium oxalate (AO) (pH = 3.0) extraction (Liu et al. 2015).

## 2.3 Soil available Cd and Cd fractionation

In terms of Cd toxicity, available Cd instead of total Cd matters. Therefore, available Cd was focused on and characterized by five methods ( $Cd_{\text{soil}}$ ,  $Cd_{\text{CaCl}_2}$ ,  $Cd_{\text{HNO}_3}$ ,  $Cd_{\text{DTPA}}$ , and  $Cd_{\text{DGT}}$ ) in this work. Both the Cd in soil pore water ( $Cd_{\text{soil}}$ ) and that is extractable by 0.01 M  $\text{CaCl}_2$  ( $Cd_{\text{CaCl}_2}$ ) are considered directly available to plants (Houba et al. 2000). In contrast, the Cd that is extractable by 0.43 M  $\text{HNO}_3$  ( $Cd_{\text{HNO}_3}$ ) or 0.005 M DTPA ( $Cd_{\text{DTPA}}$ ), two strong extractants, is considered potentially available (Zhang et al. 2016). The Cd sampled by DGT, a passive sampling process, is highly available as a DGT device functions similar to a plant root (Zhang et al. 2001).

A five-step sequential fractionation of Cd was also carried out (Tessier et al. 1979), and five fractions of Cd, exchangeable Cd (F1), carbonate-bounded Cd (F2), Fe/Mn oxide-bounded Cd (F3), organic-bounded Cd (F4), and residual Cd (F5) were obtained.

## 2.4 DGT deployment and soil solution collection

The DGT devices used in this work were purchased from Nanjing Vision Environmental Science & Technology Co., Ltd. (Nanjing, China). Before DGT deployment, 60 g of air-dried soil was weighed, placed into a 250-mL beaker, adjusted to 60% maximum water holding capacity (MWHC) with ultrapure water, and left to equilibrate for 48 h. After that, the soil was wetted to 80–100% MWHC for 24 h at room temperature (Zhang et al. 2001; Wang et al. 2014). The soil slurry was then divided into three equal aliquots and each aliquot was put into a petri dish (60-mm diameter). A DGT device

was deployed in each dish and the dishes were maintained at 25 °C for 24 h. After the retrieve of the DGT devices, the binding gels were removed and eluted with 1 mL of 1 M  $\text{HNO}_3$  for at least 24 h prior to analysis. The time-averaged concentration of Cd measured by DGT ( $Cd_{\text{DGT}}$ ) can be calculated using Eq. (1):

$$Cd_{\text{DGT}} = M\Delta g/DAt \quad (1)$$

where  $\Delta g$  is the thickness (0.92 mm) of the diffusive layer,  $D$  is the diffusion coefficient of  $\text{Cd}^{2+}$  in the diffusive layer ( $6.09 \times 10^{-6} \text{ cm}^2/\text{s}$  at 25 °C),  $A$  is the surface area ( $2.54 \text{ cm}^2$ ), and  $t$  is the deployment time (24 h). The mass ( $M$ ) of Cd accumulated in the binding gel was calculated using Eq. (2)

$$M = C_e (V_g + V_e)/f_e \quad (2)$$

where  $C_e$  is Cd concentration in the eluting solution,  $V_g$  is the volume of the binding gel (0.15 mL),  $V_e$  is the volume of eluting solution (1 mL), and  $f_e$  is elution factor with a value of 0.8 according to Luo et al. (2013).

The soil slurry in the petri dishes was transferred to centrifuge tubes and centrifuged at 4000 rpm and room temperature for 30 min for soil solution collection and  $Cd_{\text{soil}}$  determination.

## 2.5 Soil and plant Cd determination

To determine soil total Cd concentration and Cd concentrations in the root, straw, and grain, soil sample was digested with  $\text{HCl-HNO}_3\text{-HClO}_4\text{-HF}$  (Li et al. 2009) while plant sample with  $\text{HNO}_3\text{-HClO}_4$ . Soil available Cd pools were extracted with  $\text{CaCl}_2$ , DTPA, and  $\text{HNO}_3$ , the five fractions of Cd, and Cd in the soil and plant part digestion solutions were determined using flame atomic absorption spectrometry (AAS, Hitachi Z-2300, Japan);  $Cd_{\text{soil}}$ ,  $Cd_{\text{DGT}}$ , and the F4 fraction of soil Cd were determined by inductively coupled plasma mass spectrometry (ICP-MS, XSeries 2, Thermo Scientific, USA) due to low Cd concentrations.

## 2.6 Statistical analysis

SPSS statistics 23.0 and R software combined with SigmaPlot 12.0 were employed for data analysis in this study. Random forest (RF), a precise learning algorithm, was employed here to analyze the relative importance of soil properties affecting Cd accumulation in rice grains (Breiman 2001a, b).

# 3 Results and discussion

## 3.1 Soil properties

The physicochemical properties of the three different parent material-derived soils are shown in Table 1. In the

**Table 1** Physicochemical properties of the sandshale soils, limestone soils, and Quaternary red earths. The data were presented as mean ± standard deviation ( $n = 42$  for the sandshale soils,  $n = 40$  for the limestone soils, and  $n = 40$  for the Quaternary red earths)

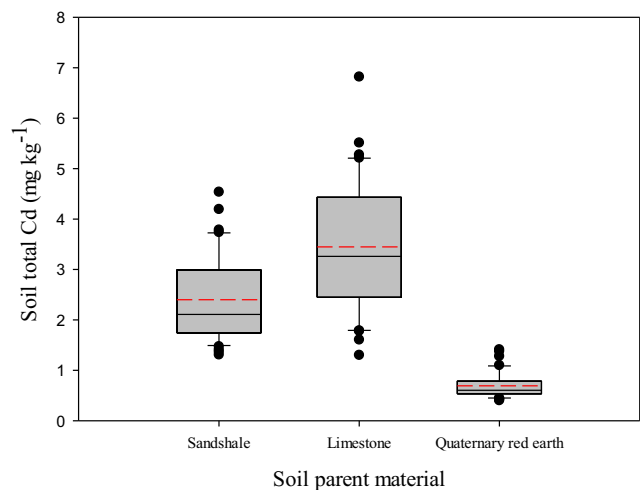
	Sandshale	Limestone	Quaternary red earth
$Fe_T$ (g $kg^{-1}$ )	12.02 ± 3.28	19.24 ± 5.52	23.28 ± 7.33
$Mn_T$ (mg $kg^{-1}$ )	0.11 ± 0.07	0.27 ± 0.21	0.12 ± 0.04
DOC (mg $kg^{-1}$ )	439.22 ± 266.19	170.38 ± 102.62	98.41 ± 39.26
pH	6.34 ± 0.72	5.89 ± 0.55	5.76 ± 0.34
CEC (cmol(+) $kg^{-1}$ )	12.7 ± 2.47	7.82 ± 2.94	9.89 ± 1.79
Sand (%)	19.35 ± 6.38	19.92 ± 9.64	26.03 ± 7.11
Silt (%)	61.83 ± 5.23	57.00 ± 8.21	44.23 ± 6.21
Clay (%)	18.82 ± 4.07	23.08 ± 8.35	29.74 ± 5.25
SOM (g $kg^{-1}$ )	73.44 ± 13.78	33.19 ± 7.40	48.57 ± 13.70
$Fe_{AO}$ (g $kg^{-1}$ )	2.55 ± 1.05	3.37 ± 1.68	5.41 ± 0.88
$Fe_{DCB}$ (g $kg^{-1}$ )	7.87 ± 3.20	14.95 ± 4.97	17.99 ± 3.92
$Mn_{AO}$ (mg $kg^{-1}$ )	52.39 ± 56.10	183.03 ± 120.73	54.76 ± 27.27
$Mn_{DCB}$ (mg $kg^{-1}$ )	66.37 ± 58.80	195.95 ± 191.38	76.28 ± 35.52

$Fe_T$ , total Fe;  $Mn_T$ , total Mn;  $Fe_{AO}$ , amorphous iron (Fe), extracted with 0.2 mol  $L^{-1}$  ammonium oxalate (pH 3.0);  $Fe_{DCB}$ , DCB-extracted Fe, extracted with dithionite-citrate-bicarbonate (DCB);  $Mn_{AO}$ , amorphous manganese (Mn), extracted with 0.2 mol  $L^{-1}$  ammonium oxalate (pH 3.0);  $Mn_{DCB}$ , DCB-extracted Mn, extracted with DCB

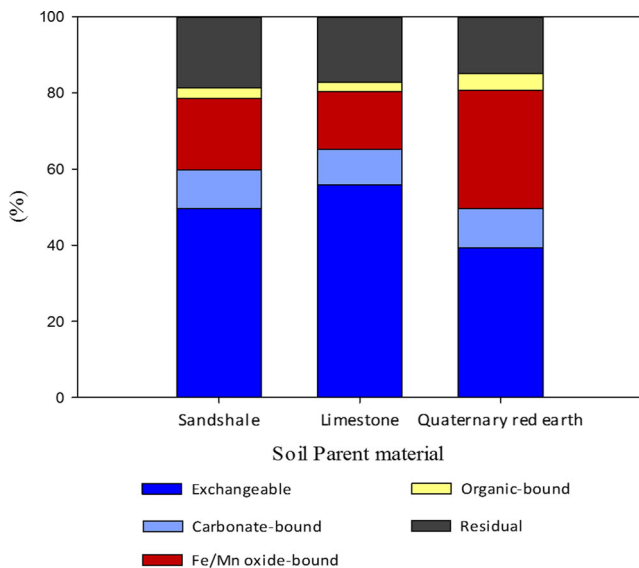
sampling areas, total Fe ( $Fe_T$ ), ammonium oxalate-extractable Fe ( $Fe_{AO}$ ), and DCB-extractable Fe ( $Fe_{DCB}$ ) were higher in the Quaternary red earths and limestone soils than in the sandshale soils.  $Fe_T$ ,  $Fe_{AO}$ , and  $Fe_{DCB}$  in the Quaternary red earths were approximately two times higher than those in the sandshale soils. In contrast, total Mn ( $Mn_T$ ), ammonium oxalate-extractable Mn ( $Mn_{AO}$ ), and DCB-extractable Mn ( $Mn_{DCB}$ ) were much higher in the limestone soils than in the Quaternary red earths or sandshale soils. The majority of the soils were weakly acidic, with a pH between 5.5 and approximately 6.5. However, the sandshale soils were slightly alkaline, with > 30% of the samples having a pH above 7. It might be due to the calciferous mountains around the sampling sites. Approximately 30% samples of limestone soils were acidic, with a pH between 5.2 and approximately 5.5, which might be related to farming history. For the Quaternary red earths, 20% of the soils were acidic, with a pH between 5.15 and approximately 5.5, while 80% of the soils were weakly acidic, with a pH between 5.5 and approximately 6.5, showing the typical red earth characteristics of low pH. SOM content of the soil samples ranged from 13.71 to 101.74 mg  $g^{-1}$ . Among the three types of soils, sandshale-derived soils had the highest SOM content (73.44 ± 13.78 mg  $g^{-1}$ ), limestone-derived soils had the lowest (33.19 ± 7.40 mg  $g^{-1}$ ). Besides, relatively high DOC concentrations were also observed in the sandshale soils. Soil particle size distribution showed that the Quaternary red earths had the highest contents of sand (0.05–2 mm) and clay (<2 mm) but the lowest content of silt (2–50 mm) among the three parent material soils. In contrast, the sandshale soils had the lowest sand and clay contents but the highest silts content.

### 3.2 Soil total Cd, soil Cd fractions and soil available cd

Total Cd of the sandshale, limestone, and Quaternary red earth soils ranged from 1.31 to 4.54 mg  $kg^{-1}$ , from 1.30 to 6.82 mg  $kg^{-1}$ , and from 0.40 to 1.41 mg  $kg^{-1}$ , respectively, with means of 2.40 ± 0.84, 3.45 ± 1.29, and 0.69 ± 0.25 mg  $kg^{-1}$ , respectively. For the limestone soil samples, it was location dependent. Total Cd of the 25 samples from Jialiao and of the 15 from Balun ranged from 2.70 to 4.21 mg  $kg^{-1}$  and from 1.30 to 2.86 mg  $kg^{-1}$ , respectively. All the soil samples had a total Cd exceeding the second grade standard of soil environment quality standard (0.3 mg  $kg^{-1}$ , GB15618-1995) (Fig. 1). The



**Fig. 1** Total Cd in the sandshale soils, limestone soils, and Quaternary red earths. The solid lines inside the box represent the sample median and mean values, respectively. The bottom (top) line of boxes is lower (upper) quartile. The lower (upper) whisker is the minimum (maximum). The full circles point to outliers



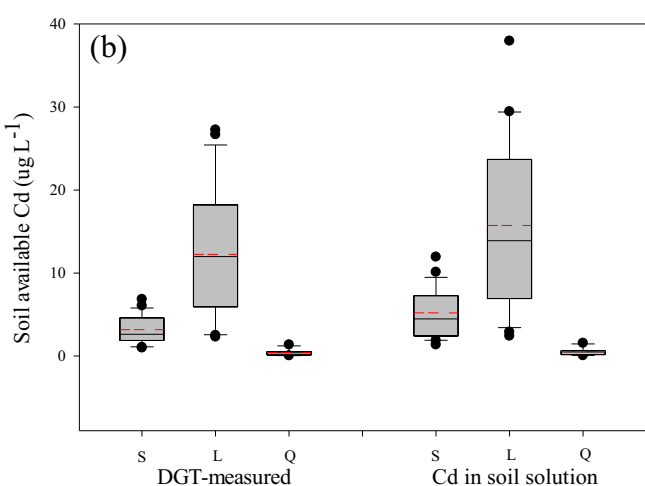
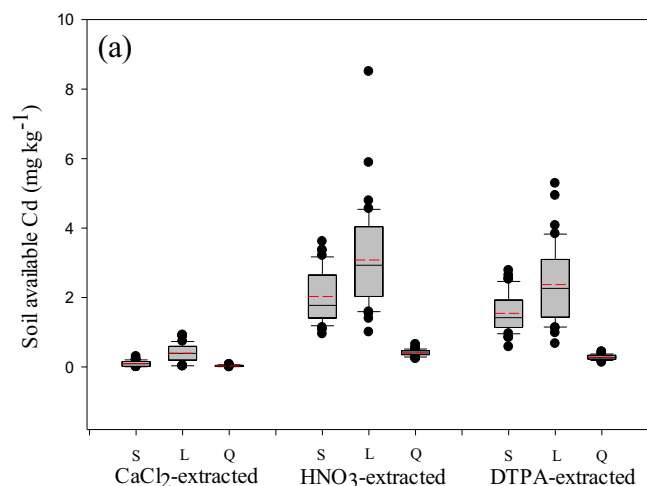
**Fig. 2** Average proportions of the five Cd fractions in total Cd of the sandshale soils, limestone soils, and Quaternary red earths

result that the limestone-derived soils had the highest total Cd among the three soils was in line with the results reported by other researchers (Zheng 1993). The possible reason is that weathering of limestone parent rock produces such soil secondary minerals as calcite, dolomite, and aragonite. These minerals are rich in divalent ions like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  whose ionic radii are close to that of Cd (0.97 Å). Therefore, the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the crystal lattice of secondary minerals could be replaced by  $\text{Cd}^{2+}$ , resulting in high Cd in limestone-derived soils (Wu et al. 2011). However, unexpectedly in this study, total Cd in the Quaternary red earth-derived soils was much lower than that in the sandshale-derived soils (Fig. 1). The surrounding calcareous mountains might have

brought secondary minerals to the sandshale soils, contributing to high Cd. In addition, differences in farming practices such as fertilization and pesticide and soil amendment application could bring different Cd input.

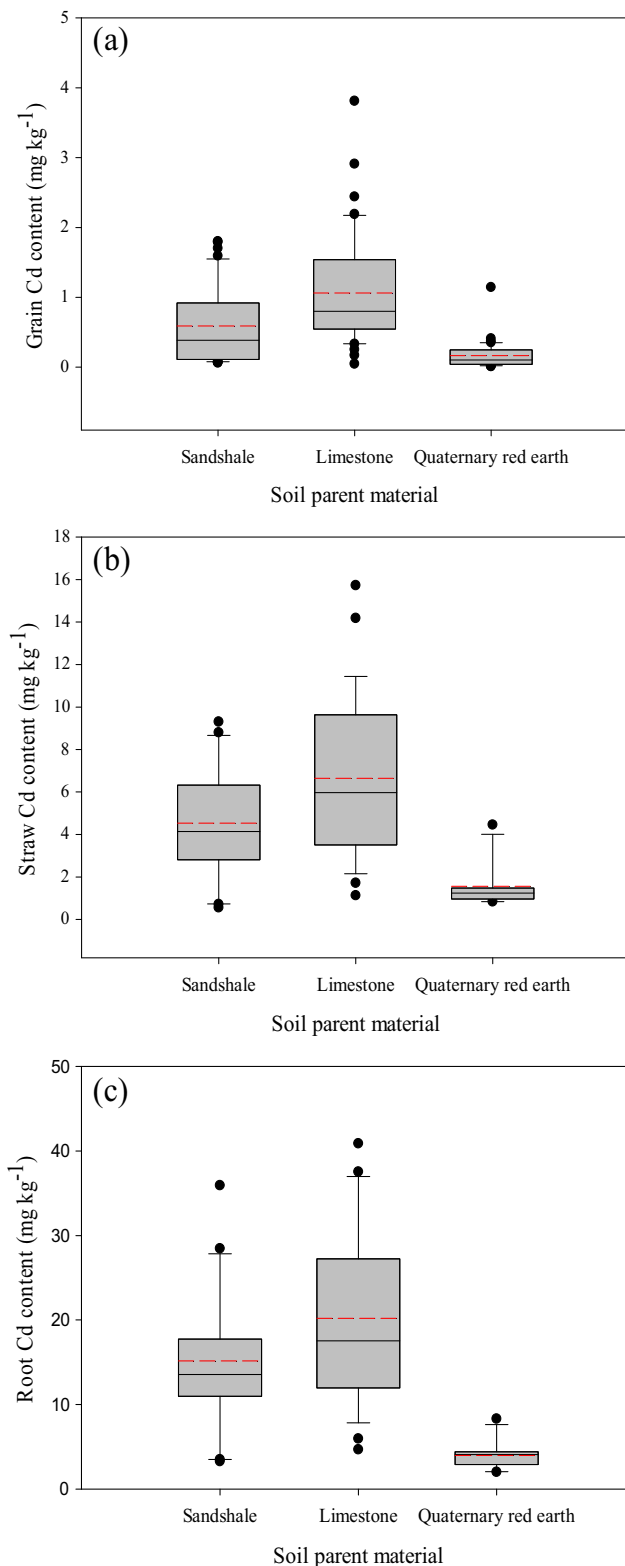
For the three types of soils, the exchangeable fraction of Cd took up a large proportion of total Cd, 50% in the sandshale soils; 56% in the limestone soils; and 39% in the Quaternary red earths on average (Fig. 2), indicating high Cd availability and high health risk of Cd in these soils as well (Kennou et al. 2015). The carbonate-bound fraction (F2) was approximately 10% of the total Cd regardless of soil parent materials. In terms of the Fe/Mn oxide-bound fraction (F3), higher proportion was found in the Quaternary red earths (31%) than in the sandshale soils (19%) and limestone soils (15%). Higher F3 proportion in the Quaternary red earths is due to the high Fe/Mn contents in these soils (Hou et al. 2013). The F3 fraction of Cd is active and available under reducing conditions due to the transformation of Fe(III) and Mn(IV) to Fe(II) and Mn(III), respectively, and the consequent release of adsorbed Cd. The organic-bound fraction (F4) in this study ranged from 2 to 4% for all the samples, the small percentage of Cd binding to organic matters may be due to its lower covalent bonding to humus, such as humic acid (Honma et al. 2015). Only 14–19% of the total Cd was of the stable residual fraction (F5), implying a great potential risk of Cd in these three parent material-derived paddy soils.

For available Cd characterized by different methods, the  $\text{CaCl}_2$ -extracted Cd was markedly smaller than the DTPA- or  $\text{HNO}_3$ -extracted Cd due to the milder effect of  $\text{CaCl}_2$  (Fig. 3). As a strong chelating agent, DTPA can extract the Fe/Mn-oxide bounded Cd and organic bounded Cd and the part of Cd adsorbed on secondary



**Fig. 3**  $\text{CaCl}_2$ -extracted,  $\text{HNO}_3$ -extracted, and DTPA-extracted Cd (a), and DGT-measured Cd and Cd in soil solution (b). The solid and dash lines inside the box represent the sample median and mean values, respectively.

The bottom (top) line of boxes is lower (upper) quartile. The lower (upper) whisker is the minimum (maximum). The full circles point to outliers. S sandshale soils, L limestone soils, Q Quaternary red earth



**Fig. 4** Cd content in the rice grains (a), straws (b), and roots (c). The solid and dash lines inside the box represent the sample median and mean values, respectively. The bottom (top) line of boxes is lower (upper) quartile. The lower (upper) whisker is the minimum (maximum). The full circles point to outliers

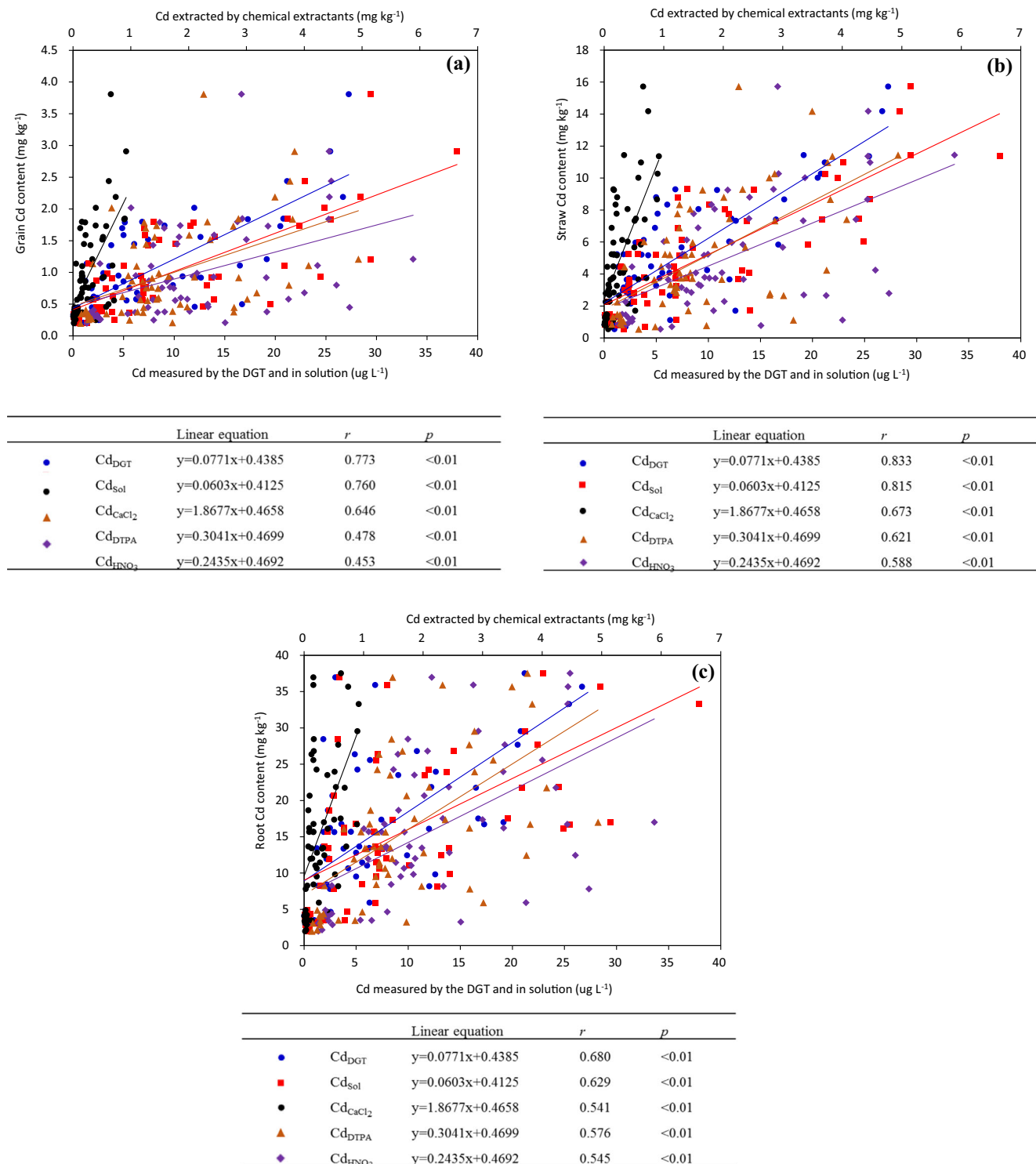
clay minerals. H<sup>+</sup> in HNO<sub>3</sub> has a strong substitution and can accelerate soil acidification, thus, promoting the dissolution of Cd. The part of Cd that can be extracted by DTPA or HNO<sub>3</sub> is potentially bioavailable (Zhang et al. 2016). In this study, the HNO<sub>3</sub>-extracted Cd was even higher than the DTPA-extracted Cd, which was in line with previous results (Zhang et al. 2016). Cd<sub>DGT</sub> and Cd<sub>sol</sub> were obtained without using extractants. Similar to Cd<sub>sol</sub>, high Cd<sub>DGT</sub> was found in the limestone soils, about 3 and 30 times that in the sandshale soils and the Quaternary red earths, respectively.

### 3.3 Cd accumulation and distribution in rice

The total Cd in the rice grains harvested from the sandshale soils, limestone soils, and Quaternary red earths ranged from 0.06 to 1.80 mg kg<sup>-1</sup>, 0.05 to 3.52 mg kg<sup>-1</sup>, and 0.01 to 1.14 mg kg<sup>-1</sup>, respectively, with mean ± SD values of 0.59 ± 0.53, 1.04 ± 0.79, and 0.16 ± 0.20 mg kg<sup>-1</sup>, respectively (Fig. 4a). In terms of Cd concentration, the plant parts were in the following decreasing order: root > straw > grain (Fig. 4). This demonstrated that most of the Cd in the rice plants were in the roots and straws instead of in the edible part of grains. Particularly, Cd concentration in the roots was on average 2~3 and 10~17 times that in the straws and grains, respectively, and Cd concentration in the straws was on average 2~5 times that in the grains. High Cd concentration was found in the grains grown in the limestone soils while low Cd content in the Quaternary red earths (Fig. 4). Even though Cd concentration in the rice grains was far lower than in the straws and roots, still, Cd concentration in 67% of the rice grain samples from the sandshale soils exceeded the maximum allowable amounts of Cd (0.2 mg kg<sup>-1</sup>, GB 2762–2012). The number was even alarming for rice grains harvested from the limestone soils and Quaternary red earths, which was 95 and 28%, respectively.

### 3.4 Relationship between soil available Cd and Cd accumulation in rice grains

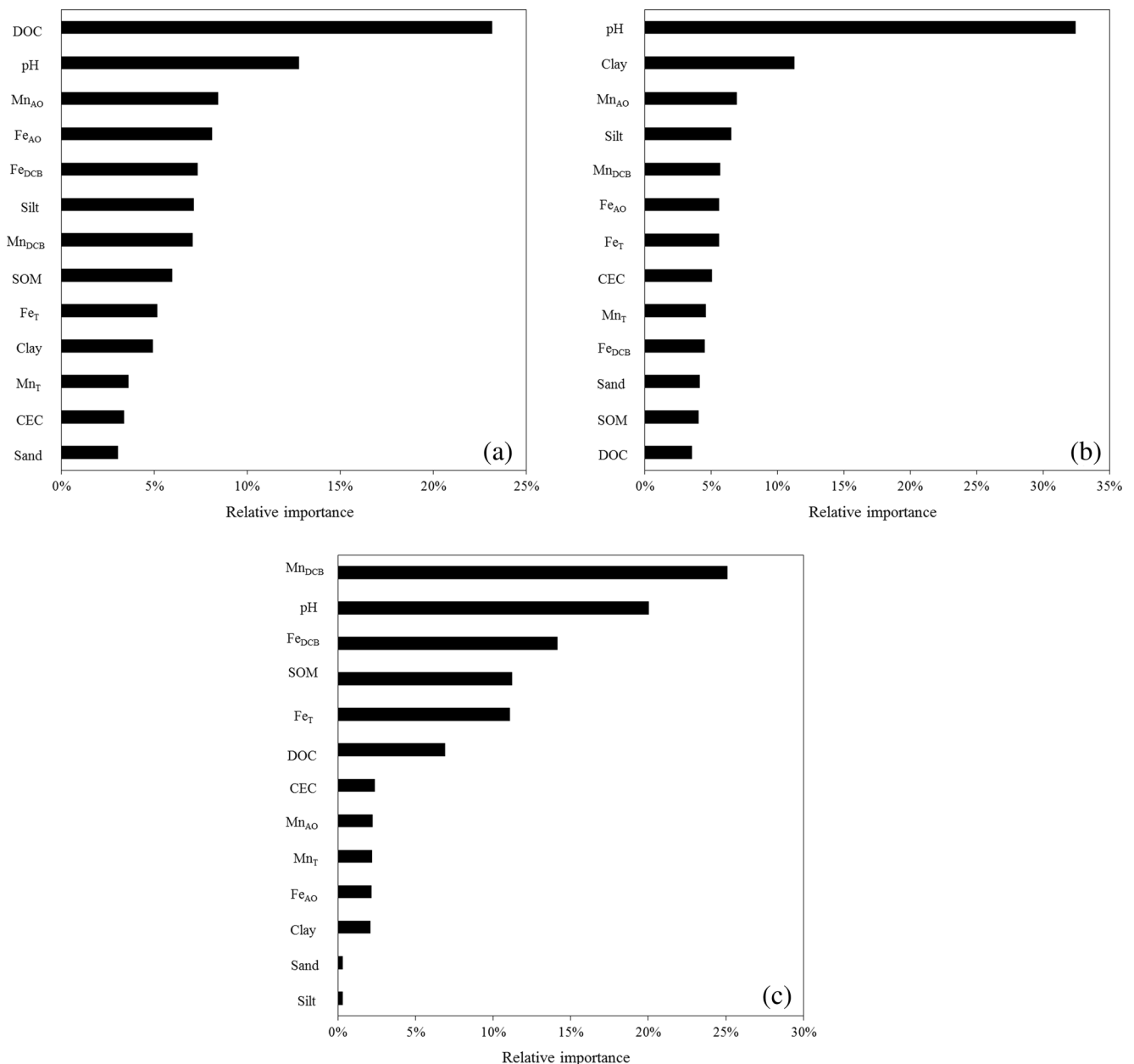
Cd concentration in the rice grains (Cd<sub>grain</sub>), straws (Cd<sub>straw</sub>), or roots (Cd<sub>root</sub>) was significantly correlated (*p* < 0.01) with Cd<sub>DGT</sub> and Cd<sub>sol</sub>, as shown in Fig. 5. The correlation coefficients (*r*) between Cd<sub>grain</sub> and Cd<sub>DGT</sub> or Cd<sub>sol</sub> were 0.773 and 0.760, respectively. The correlation coefficients (*r*) between Cd<sub>straw</sub> and Cd<sub>DGT</sub> or Cd<sub>sol</sub> were 0.833 and 0.815, respectively. The correlation coefficients (*r*) between Cd<sub>root</sub> and Cd<sub>DGT</sub> or Cd<sub>sol</sub> were 0.680 and 0.829, respectively. As Cd is a non-essential toxic heavy metal to plants, it is expected that Cd uptake by plants is a passive process. This explains the above significant relationship. Moreover, significant correlations (*p* < 0.01) were observed between Cd in tissues (Cd<sub>grain</sub>, Cd<sub>straw</sub> or Cd<sub>root</sub>)



**Fig. 5** Correlation between Cd content in rice grains (a), straws (b), and roots (c) and soil available cd (, DGT-measured;, Cd in soil solution;,  $CaCl_2$ -extracted;,  $HNO_3$ -extracted; and, DTPA-extracted) in the three parent material-derived paddy soils

and the Cd available pools extracted by 0.05 M  $CaCl_2$ , 0.43 M  $HNO_3$ , and 0.005 M DTPA. In comparison, the  $HNO_3$  and DTPA are too strong to reflect the passive uptake process of plants. Thus, the correlation coefficients (*r*) between  $Cd_{grain}$ ,  $Cd_{straw}$ , or  $Cd_{root}$  and

$CaCl_2$ -,  $HNO_3$ -, or DTPA-extracted Cd were lower than that between Cd in tissues ( $Cd_{grain}$ ,  $Cd_{straw}$ , or  $Cd_{root}$ ) and  $Cd_{DGT}$  or  $Cd_{sol}$ . Both  $Cd_{DGT}$  and  $Cd_{sol}$  showed good correlations with the Cd concentration in plant tissues ( $Cd_{grain}$ ,  $Cd_{straw}$ , or  $Cd_{root}$ ), indicating that DGT



**Fig. 6** Importance scores of soil properties in influencing Cd accumulation in rice grains based on random forest (RF) analyses in the sandshale soils (a), limestone soils (b), and Quaternary red earths (c). Fe<sub>T</sub> total Fe; Mn<sub>T</sub>total Mn; Fe<sub>AO</sub> amorphous Fe, extracted with 0.2 mol L<sup>-1</sup>

ammonium oxalate (pH 3.0); Fe<sub>DCB</sub> DCB-extracted Fe; Mn<sub>AO</sub> amorphous Mn, extracted with 0.2 mol L<sup>-1</sup> ammonium oxalate (pH 3.0); Mn<sub>DCB</sub> DCB-extracted Mn

method and extraction of soil pore water provided better measurements of labile Cd concentrations compared to the other three extraction methods.

The highest correlations were found between Cd in plant tissues (Cd<sub>grain</sub>, Cd<sub>straw</sub>, or Cd<sub>root</sub>) and Cd<sub>DGT</sub> in the three parent material-derived soils. This indicated that DGT was the best method to assess Cd uptake by rice in this study. In the study of Williams et al. (2012), Cd<sub>DGT</sub> accurately reflected Cd accumulation in grains. Wang et al. (2017) reported that Cd bioavailability was also well assessed by DGT in fields cultivated with wheat and maize.

### 3.5 Quantitative importance of factors affecting Cd accumulation in rice grains

Substantial studies have noted that Cd accumulation in rice grains is governed not only by rice variety but soil physicochemical characters such as soil pH, SOM, DOC, Fe/Mn oxides, etc. (Muehe et al. 2013a, b; Yu et al. 2016; Suda and Makino 2016; Li et al. 2017). These properties influence the solubility and activity of Cd, and thus impact Cd uptake by rice. Random forest (RF) is a precise learning algorithm (Breiman 2001a, b). RF was employed here to assess the relative importance of soil properties



affecting Cd accumulation in rice grains. As shown in Fig. 6a, of the sandshale soil properties, DOC and pH were the most important factors that affected Cd accumulation in rice grains, with an importance score of about 23 and 13%, respectively. The other soil properties such as  $\text{Fe}_{\text{AO}}$ ,  $\text{Mn}_{\text{AO}}$ , and clay played a less important role, with none of their importance scores higher than 9%. As for the limestone soils (Fig. 6b), pH was a far-leading factor influencing Cd accumulation in the rice grains, with an importance score up to 32%. Following pH, clay showed an importance score of 11%. The scores of the other factors were small and ranged narrowly from merely 4 to 7%. For the Quaternary red earths (Fig. 6c), the five factors of  $\text{Mn}_{\text{DCB}}$ , pH,  $\text{Fe}_{\text{DCB}}$ , SOM, and  $\text{Fe}_{\text{T}}$  made up a combined score of about 82%, with the scores of the other factors ranging from 0.3 to 7%. As can be seen that in all these three soils of different parent materials, pH was an important factor influencing Cd accumulation in the rice grains, which is in line with the results reported in the literature (Zeng et al. 2011; Yu et al. 2016). This is mainly due to the influence of pH on the dissolution or precipitation of compounds. The sandshale soils had a high DOC content which might result from farming practices such as organic fertilizer application. DOC is rich in reactive functional groups such as carboxyl, alcoholic hydroxyl, phenolic hydroxyl, and amino groups, on which Cd can bind to. Consequently, Cd in soil solution was high, which is favorable for plant uptake (He et al. 2017). Clay, an important sorption component, can reduce the chemical-extractable fraction and in turn the bioavailability of Cd in soils (Xu et al. 2017). It is generally known that Fe/Mn contents are high in Quaternary red earths and as can be seen in Fig. 2 that Fe/Mn oxide-bound Cd took up a large proportion of the total Cd in the Quaternary red earths. Transformation of Fe/Mn species can greatly affect the availability of other elements including Cd (Suda and Makino 2016). This explains why both  $\text{Mn}_{\text{DCB}}$  and  $\text{Fe}_{\text{DCB}}$  had high importance scores in the Quaternary red earths in terms of Cd accumulation in rice grains (Fig. 6c).

## 4 Conclusions

All the 122 soil samples of three parent materials and from four sites in Guangxi, China had a total Cd content (0.40–6.82  $\text{mg kg}^{-1}$ ) exceeding the maximum permissible concentration (0.3  $\text{mg kg}^{-1}$ ) for soils. Cd content in the rice grains ranged from 0.01 to 3.81  $\text{mg kg}^{-1}$ , with 67, 95, and 28% of the grains harvested from the sandshale soils, limestone soils, and Quaternary red earths having a Cd content exceeded the maximum allowable amount (0.2  $\text{mg kg}^{-1}$ ) for grains. These indicate that the sampling sites pose a great potential risk to the ecosystem and to human health through the food chain. Of the available Cd characterized by the five methods, Cd measured by DGT best reflected Cd bioavailability, being significantly and positively related to Cd content in the rice grains. Based on RF analysis, DOC and pH were the most important factors

influencing Cd accumulation in the rice grains harvested from the sandshale soils, while pH and clay the limestone soils and  $\text{Mn}_{\text{DCB}}$  and pH the Quaternary red earths. This demonstrates that as an important soil property, pH plays an important role in Cd bioavailability in the three soils of different parent materials. Measures can be taken to regulate soil pH so as to reduce Cd bioavailability and in turn Cd transfer to and accumulation in plants. In contrast, measures to change DOC, clay, or Fe/Mn content or species so as to reduce Cd availability should be soil type-dependent as the importance scores of these soil properties vary greatly in different soils.

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## References

- Adriano DC (2001) Trace elements in terrestrial environments. Trace elements in terrestrial environments. Springer New York, pp 219–261
- Breiman L (2001a) Random forests. *Mach Learn* 45:5–32
- Breiman L (2001b) Statistical modeling: the two. *Cultures* 16:199–215
- Chen JS, Wang FY, Li XD, Song JJ (2000) Geographical variations of trace elements in sediments of the major rivers in eastern China. *Environ Geol* 39:1334–1340
- Davison W, Zhang H (1994) In-situ speciation measurements of trace components in natural waters using thin-films gels. *Nature* 9:1–13
- Davison W, Zhang H (2012) Progress in understanding the use of diffusive gradients in thin films (DGT)? Back to basics. *Environ Chem* 9:1–13
- He SR, Lu Q, Li WY, Ren ZL, Zhou Z, Feng X, Zhang YL, Li YT (2017) Factors controlling cadmium and lead activities in different parent material-derived soils from the Pearl River Basin. *Chemosphere* 182:509–516
- Honma T, Ohba H, Makino T, Ohyama T (2015) Relationship between cadmium fractions obtained by sequential extraction of soil and the soil properties in contaminated and uncontaminated paddy soils. *J Chem* 6:1–9
- Hou DK, He J, Lü CW, Ren LM, Fan QY, Wang JH, Xie ZL (2013) Distribution characteristics and potential ecological risk assessment of heavy metals (Cu, Pb, Zn, Cd) in water and sediments from Lake Dalinouer, China. *Ecotox Environ Safe* 93:135–144
- Houba VJG, Temminghoff EJM, Gaikhorst GA, van Vark W (2000) Soil analysis procedures using 0.01 M calcium chloride as extraction reagent. *Commun Soil Sci Plan* 31(9–10):1299–1396
- Kennou B, El Meray M, Romane A, Arjouni Y (2015) Assessment of heavy metal availability (Pb, Cu, Cr, Cd, Zn) and speciation in contaminated soils and sediment of discharge by sequential extraction. *Environ Earth Sci* 74:5849–5858
- Li H, Luo N, Li YW, Cai QY, Li HY, Mo CH, Wang MH (2017) Cadmium in rice: transport mechanisms, influencing factors, and minimizing measures. *Environ Pollut* 2:2–9
- Li YT, Becquer T, Dai J, Quantin C, Benedetti MF (2009) Ion activity and distribution of heavy metals in acid mine drainage polluted subtropical soils. *Environ Pollut* 157:1249–1257
- Liu YQ, Du QY, Wang Q, Yu HY, Liu JF, Tian Y, Chang CY, Lei J (2017) Causal inference between bioavailability of heavy metals and environmental factors in a large-scale region. *Environ Pollut* 3:1–9
- Liu CP, Yu HY, Liu CS, Li FB, Xu XH, Wang Q (2015) Arsenic availability in rice from a mining area: is amorphous iron oxide-bound arsenic a source or sink? *Environ Pollut* 199:95–101

- Luo J, Zhang H, Davison W, McLaren RG, Clucas LM, Ma LQ, Wang X (2013) Localised mobilisation of metals, as measured by diffusive gradients in thin-films, in soil historically treated with sewage sludge. *Chemosphere* 90:464–470
- Ministry of Environmental Protection of China (1990) Chinese environmental monitoring station background concentrations of elements in Chinese soils (in Chinese). Chinese Environmental Science Publisher, Beijing
- Muehe EM, Adaktylou IJ, Obst M, Zeitvogel F, Behrens S, Planer-Friedrich B, Kraemer U, Kappler A (2013a) Organic carbon and reducing conditions lead to cadmium immobilization by secondary Fe mineral formation in a pH-neutral soil. *Environ Sci Technol* 47:13430–13439
- Muehe EM, Obst M, Hitchcock A, Tyliczszak T, Behrens S, Schröder C, Byrne JM, Michel FM, Krämer U, Kappler A (2013b) Fate of Cd during microbial Fe(III) mineral reduction by a novel and Cd-tolerant geobacter species. *Environ Sci Technol* 47:14099–14109
- Nookabkaew S, Rangkadilok N, Prachoom N, Satayavivad J (2016) Concentrations of trace elements in organic fertilizers and animal manures and feeds and cadmium contamination in herbal tea (*Gynostemma pentaphyllum* Makino). *J Agr Food Chem* 64:3119–3126
- Rafiq MT, Aziz R, Yang X, Xiao W, Rafiq MK, Ali B, Li T (2014) Cadmium phytoavailability to rice (*Oryza sativa* L.) grown in representative Chinese soils. A model to improve soil environmental quality guidelines for food safety. *Ecotoxicol Environ Saf* 103:101–107
- Sebastian A, Prasad MNV (2014) Cadmium minimization in rice. A review. *Agron Sustain Dev* 34:155–173
- Suda A, Makino T (2016) Functional effects of manganese and iron oxides on the dynamics of trace elements in soils with a special focus on arsenic and cadmium: a review. *Geoderma* 270:68–75
- Tan XP, Liu YJ, Yan KH, Wang ZQ, Lu GN, He YK, He WX (2017) Differences in the response of soil dehydrogenase activity to Cd contamination are determined by the different substrates used for its determination. *Chemosphere* 169:324–332
- Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem Soc* 51:844–851
- Tsukahara T, Ezaki T, Moriguchi J, Furuki K, Shimbo S, Matsuda-Inoguchi N, Ikeda M (2003) Rice as the most influential source of cadmium intake among general Japanese population. *Sci Total Environ* 305:41–51
- Vig K, Megharaj M, Sethunathan N, Naidu R (2003) Bioavailability and toxicity of cadmium to microorganisms and their activities in soil: a review. *Adv Environ Res* 8:121–135
- Wang JJ, Bai LY, Zeng XB, Su SM, Wang YN, Wu CX (2014) Assessment of arsenic availability in soils using the diffusive gradients in thin films (DGT) technique—a comparison study of DGT and classic extraction methods. *Environ Sci Process Impacts* 16:2355–2361
- Wang PF, Liu C, Yao Y, Wang C, Wang T, Yuan Y, Hou J (2017) Comparison of *in situ* DGT measurement with *ex situ* methods for predicting cadmium bioavailability in soils with combined pollution to biotas. *Water Sci Technol* 75:2171–2178
- Williams PN, Zhang H, Davison W, Zhao S, Lu Y, Dong F, Zhang L, Pan AQ (2012) Evaluation of *in situ* DGT measurements for predicting the concentration of Cd in Chinese field-cultivated rice: impact of soil Cd:Zn ratios. *Environ Sci Technol* 46:8009–8016
- Wu ZH, He MC, Lin CY, Fan YH (2011) Distribution and speciation of four heavy metals (Cd, Cr, Mn and Ni) in the surficial sediments from estuary in daliao river and yingkou bay. *Environ Earth Sci* 63:163–175
- Xu Y, Liang XF, Xu YM, Qin X, Huang QQ, Wang L, Sun YB (2017) Remediation of heavy metal-polluted agricultural soils using clay minerals: a review. *Pedosphere* 27:193–204
- Yu HY, Liu C, Zhu J, Li FB, Deng D, Wang Q, Liu C (2016) Cadmium availability in rice paddy fields from a mining area: the effects of soil properties highlighting iron fractions and pH value. *Environ Pollut* 209:38–45
- Zeng FR, Ali S, Zhang HT, Ouyang YN, Qiu BY, Wu FB, Zhang GP (2011) The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. *Environ Pollut* 159:84–91
- Zhang CS, Ding SM, Xu D, Tang Y, Wong MH (2014) Bioavailability assessment of phosphorus and metals in soils and sediments: a review of diffusive gradients in thin films (DGT) [J]. *Environ Monit Assess* 186:7367–7378
- Zhang H, Zhao FJ, Sun B, Davison W, Mcgrath SP (2001) A new method to measure effective soil solution concentration predicts copper availability to plants. *Environ Sci Technol* 35:2602–2607
- Zhang LP, Sun Q, Ding SM, Cheng X, Liu Q, Zhang CS (2017a) Characterization of arsenic availability in dry and flooded soils using sequential extraction and diffusive gradients in thin films (DGT) techniques. *Environ Sci Pollut Res* 24:15727–15734
- Zhang S, Song J, Gao H, Zhang Q, Lv M, Wang S, Liu G, Pan YY, Christie P, Sun WJ (2016) Improving prediction of metal uptake by Chinese cabbage (*Brassica pekinensis* L.) based on a soil-plant stepwise analysis. *Sci Total Environ* 569–570:1595–1605
- Zhang YL, Wang LY, Li WY, Xu HJ, Shi YC, Sun YT, Cheng X, Chen XY, Li YT (2017b) Earthworms and phosphate-solubilizing bacteria enhance carbon accumulation in manure-amended soils. *J Soils Sediments* 17:220–228
- Zheng W (1993) Background value of some heavy metal elements in agricultural soil environment in northeast Guangxi. *Rural Eco-Environ* 4:39–42 (Chinese)
- Zhang H, Davison W (1995) Performance characteristics of diffusion gradients in thin films for the *in situ* measurement of trace metals in aqueous solution [J]. *Anal Chem* 67:3391–3400