Cadmium Bioavailability and Accumulation in Rice Grain are Controlled by pH and Ca in Paddy Soils with High Geological Background of Transportation and Deposition

Chen Jiale[1] · Zheng Chao[1] · Ruan Jinzhao[1] · Zhang Chunhua[2] · Ge Ying[1]

Abstract

Cadmium (Cd) threatens rice quality and human health, yet this risk remains uncertain in paddy fields with high geological background of transportation and deposition. In this study, we collected 31 pairs of soil and rice grain samples in Doumen and Xinhui Districts in Guangdong province, China and investigated which factors controlled Cd bioavailability in soil and accumulation in rice. Soil samples were mostly acidic and contained a range of organic matter. Total Cd in soil varied from 0.10 to 1.03 $mg\,kg^{-1}$ and was positively correlated with those of calcium (Ca), manganese (Mn) and iron (Fe), suggesting that these elements shared same sources and Cd was most likely originated from parent material. The activity ratio (AR, $CaCl_2$-extractable Cd/soil Cd) and bioconcentration factor (BCF, rice grain Cd/soil Cd) of Cd were negatively correlated with soil pH. The coupling relationship between soil and rice grain Cd could be described by a linear model, which was used to predict soil Cd threshold values to keep rice grain Cd concentration from exceeding the Chinese limit ($0.2\,mg\,kg^{-1}$). In summary, Cd pollution was not very severe in the paddy soils of studied area but the risk could not be neglected when soil was acidified, which could increase Cd bioavailability and accumulation in rice grain.

Keywords High geological background · Paddy field · Rice · Cd · pH · Ca

With the rapid development of the economy, heavy metal pollution has become a serious environmental issue (Liu et al. 2015), which is contributed by anthropogenic (such as mining, industrial and agricultural activities) (Cai et al. 2015; Pietrzykowski et al. 2018) and natural sources (e.g., weathering, transportation, deposition) (Wong et al. 2002). Among various heavy metals, cadmium (Cd) has a strong toxicity and its accumulation in rice seriously threatens human health (Kadirvelu et al. 2001; Brus et al. 2009; Gu et al. 2014; Sebastian and Prasad 2014; Hu et al. 2016).

Chen Jiale and Zheng Chao contributed equally.

✉ Ge Ying
  yingge711@njau.edu.cn

[1] College of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing 210095, China

[2] Demonstration Laboratory of Element and Life Science Research, Laboratory Centre of Life Science, College of Life Science, Nanjing Agricultural University, Nanjing 210095, China

High geological background (HGB), which is characterized by unusually high levels of heavy metals in soils and their parent materials, commonly exists in many areas around the globe (Facchinelli et al. 2001; Zhou et al. 2008; Rodríguez-Oroz et al. 2017; Wen et al. 2020). For example, 88% of chromium (Cr) and 68% of nickel (Ni) in the soils sampled from areas with basalt rocks exceeded the soil quality criteria (Jiang and Wang 2020). On the other hand, metal bioavailability in such soils is often not very high because of soil alkalinity or metal binding in mineral structures, leading to low uptake of metals by plants. For instance, bioconcentration factor (BCF) of Cd in soils with HGB in Guangxi province was three times lower than that in soils polluted by human activities (Chen et al. 2016; Tang et al. 2018). However, the potential risks associated with soils with HGB cannot be neglected, since the metals may be activated by changes of soil properties such as pH (Wen et al. 2020).

Transportation and deposition are common natural processes to form HGB in soils. Pearl River Delta (PRD) in Guangdong province, China is a typical region of HGB. Here the soil parent materials are mainly river sediments migrated from the upstream karst areas in Guangxi province

(Chen et al. 2020). Moderate to high levels of Cd in soils have been reported in PRD (Lai et al. 2005), where average sediment Cd (0.24 mg kg^{-1}) could be twice as high as that in the Yangtze River Delta (Liu et al. 2012), or reached 0.5 mg kg^{-1} due to over-exploitation in upstream mining areas (Wen et al. 2020). High density of river network in this region is another factor to generate potential ecological risks (Hou 2019).

It is well known that Cd bioavailability may be affected by various physicochemical properties of soils such as pH, organic matter, CEC, total metals, macronutrients, etc. (McBride 2002; Zu et al. 2003; Römkens et al. 2009; Sarwar et al. 2010; Li et al. 2017). However, it is still unclear which factors control the Cd bioavailability in soils with HGB of transportation and deposition, making it difficult to assess the risks of Cd pollution and predict soil threshold Cd content for safe rice production. Therefore, in this study we collected paired soil and rice samples in southwestern part of PRD, and determined soil properties, Cd contents in soil and rice grain. The objectives of study are: (1) to reveal main controlling factors of Cd bioavailability in soils; (2) to predict the threshold values of soil Cd to keep rice grain from contamination.

Methods and Materials

Thirty-one pairs of soil and rice grain samples were collected in the area of Doumen and Xinhui Districts (Fig. 1), which are located in the southwest of PRD. The sampling area has abundant heat, sunlight, rainfall (~ 1600 mm per year) (Wang et al. 2014) and large size of plains originated from sediment deposition.

The sampling locations were in rural area, where no mining or industrial activities were present. In July 2018, 31 pairs of rhizosphere soil and rice grain samples were collected, with the coordinates recorded by GPS. In each paddy, five soil samples were taken and combined as a bulk sample for this location. The samples were reduced to about 1 kg by quartering method before taking back to laboratory.

Soil samples were air-dried, ground and passed through 10-mesh nylon sieves for pH, 20-mesh for available Cd and 100-mesh for soil organic matter (SOM) and elemental analyses. Rice grain samples were oven-dried, ground and stored under the same conditions as soils. The soil pH was measured by potentiometer (sartorius PB-21) after mixing the sample with water with a ratio of 1:2.5 (Lu 2000). SOM was digested with $K_2Cr_2SO_4$ and H_2SO_4 and determined by spectrometer (METASH UV-5300) (Lu 2000). Available Cd in soil samples was extracted by 0.01M $CaCl_2$ solution (Zhang 2011) and determined by inductively coupled plasma emission spectrometer (ICP-OES, PerkinElmer Optima 8000).

For total metal analysis, the 100-mesh soil and rice grain samples were respectively digested by $HCl–HNO_3–HF–HClO_4$ (10:5:5:3) and $HNO_3–HClO_4$ (4:1) (Lin et al. 2015; Tian and Zheng 2017). Cadmium was determined by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer NexION 2000). Aluminum, Ca, Fe and Mn were determined by ICP-OES (PerkinElmer Optima 8000). Certified reference materials (CRM, soil GBW07453 (GSS-24); plant GBW07603 (GSV-2)) were used in quality control and the calculated recovery rate of all elements in 80%–120%.

Fig. 1 Location of the sampling points
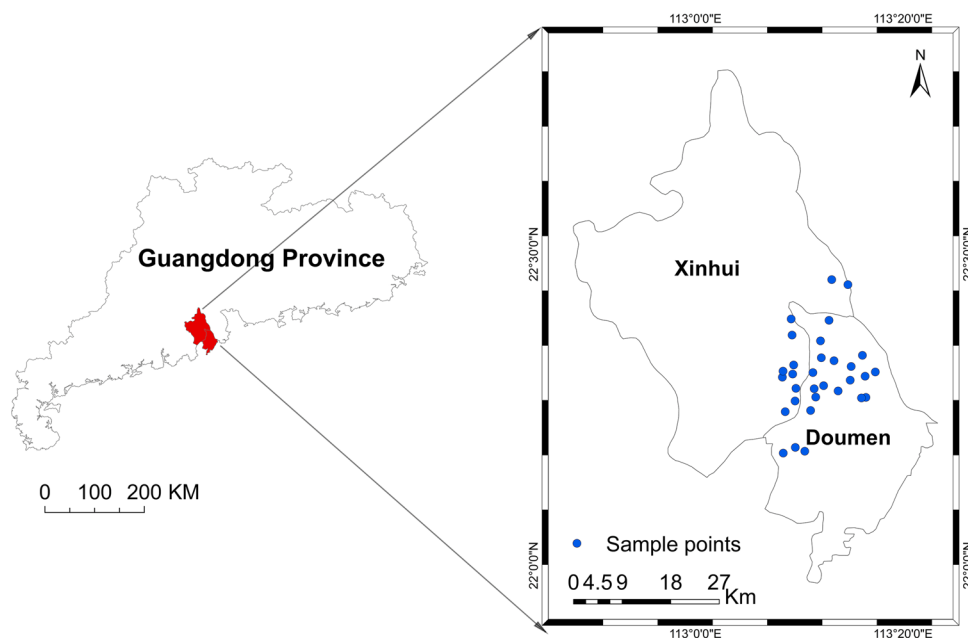
The activity of Cd in soil can be described with activity ratio (AR) (Pan et al. 1999), which is calculated by the following formula:

$$AR = \frac{Ava\_Cd}{Soil\_Cd} \qquad (1)$$

where Ava_Cd and Soil_Cd are available Cd and total Cd content in soil, respectively.

Bioconcentration factors (BCF) is the ratio of Cd content in rice grain to that in soil (Wen et al. 2020) and is expressed using the following formula:

$$BCF = \frac{Grain\_Cd}{Soil\_Cd} \qquad (2)$$

where Grain_Cd and Soil_Cd are Cd content in rice grain and in soil, respectively.

Data of this study were analyzed with Excel2019. Linear and nonlinear models were constructed to describe relationships among various parameters. Graphs were prepared using Origin 2019b.

Results and Discussion

Most of the soil samples were acidic (Macías and Camps-Arbestain 2020), as the median pH was around 5.5 (Table 1), although a few soils had pH higher than 7. The average of SOM was around 3.5%, with a coefficient of variance (CV) of 8.45%.

For Cd in soil, the average value was 0.4 $mg\,kg^{-1}$, which is about 10 times the background value in this region (0.056 $mg\,kg^{-1}$) (MEP 1990), and the range was relatively large (0.1–1.03 $mg\,kg^{-1}$). Ava_Cd was about 1/10 of Soil_Cd and its CV was higher than that of Soil_Cd. Soil Al, Fe, Ca, Mn were all lower than the values reported in the upstream karst areas (Wen et al. 2020). The average values of Grain_Cd was 0.17 $mg\,kg^{-1}$, which was close to the Chinese limit for Cd concentration in rice grain (0.2 $mg\,kg^{-1}$).

The high Cd content in soils may be related to the formation process of the PRD, where a dense river network has emerged due to the interaction of three transgressions and regressions (Huang 1982). These processes have caused Cd migration and deposition here with the river (Lai et al. 2005; Hou 2019; Chen et al. 2020), forming HGB with Soil_Cd in this region (Liu et al. 2012). In addition, average soil Ca content (1.77 $g\,kg^{-1}$, Table 1) was also higher than the background value (0.6 $g\,kg^{-1}$, MEP 1990), because its carriers, such as illite and kaolinite, had higher Ca abundance in the parent material composition (Lan et al. 1988).

Significantly positive relationships were observed between total Cd and Cd, Mn, Fe contents ($R^2 > 0.7$, $P < 0.05$) (Fig. 2). These results indicated that soil Cd in the sampling locations was likely originated from the same source with Ca, Mn and Fe. Cadmium may come from minerals containing Ca, Fe and Mn such as stalactites, or iron and manganese oxides in upstream areas such as Guangxi, where Cd background value is 0.246 $mg\,kg^{-1}$ (MEP 1990).

Along with weathering of carbonate, basalt and black shale rocks, heavy metals are released into rivers, flowed to downstream and subsequently deposited in sediments (Qu et al. 2020). This phenomenon has been reported by Wu et al. (2020a), who found that Cd content in soils around Diaojiang River (a tributary of upper reaches of Pearl River) was two orders of magnitude higher than the background value. Owing to the HGB, Cd was shown to have a severe ecological risk in soils of Xijiang River valley in Yunnan and Guizhou provinces (Wu et al. 2020b). However, in recent years, human activities like mining, industrial and sewage discharge also resulted in increase of heavy metal levels in the sediments of Pearl River (Ip et al. 2004). Nevertheless, natural processes are still the main controlling factors for Soil_Cd in the PRD (Geng et al. 2015).

The correlation between pH and AR was clearly negative ($R^2 > 0.99$, $P < 0.05$) (Fig. 3a). However, the correlation between SOM and AR was weak, indicating that pH was the main controlling factor for the Cd activity in soils. The Ava_Cd extracted by CaCl$_2$ solution (0.01 $mol\,L^{-1}$)

Table 1 Descriptive analyses for the parameters of soil and rice samples

| Sample	Parameters	Mean	Median	Minimum value	Maximum value	Coefficient of variance (%)
Soil	pH	5.75	5.49	4.72	7.52	10.56
	SOM (%)	3.49	3.58	2.63	3.92	8.45
	Soil_Cd ($mg\,kg^{-1}$)	0.40	0.40	0.10	1.03	53.38
	Ava_Cd ($mg\,kg^{-1}$)	0.03	0.02	0.004	0.12	83.11
	Soil_Al ($g\,kg^{-1}$)	44.78	45.51	13.85	97.53	41.20
	Soil_Fe ($g\,kg^{-1}$)	35.07	41.11	4.73	53.00	40.37
	Soil_Ca ($g\,kg^{-1}$)	1.77	1.52	0.06	3.93	64.43
	Soil_Mn ($g\,kg^{-1}$)	0.36	0.35	0.07	0.76	55.01
Rice	Grain_Cd ($mg\,kg^{-1}$)	0.17	0.14	0.02	0.35	58.80
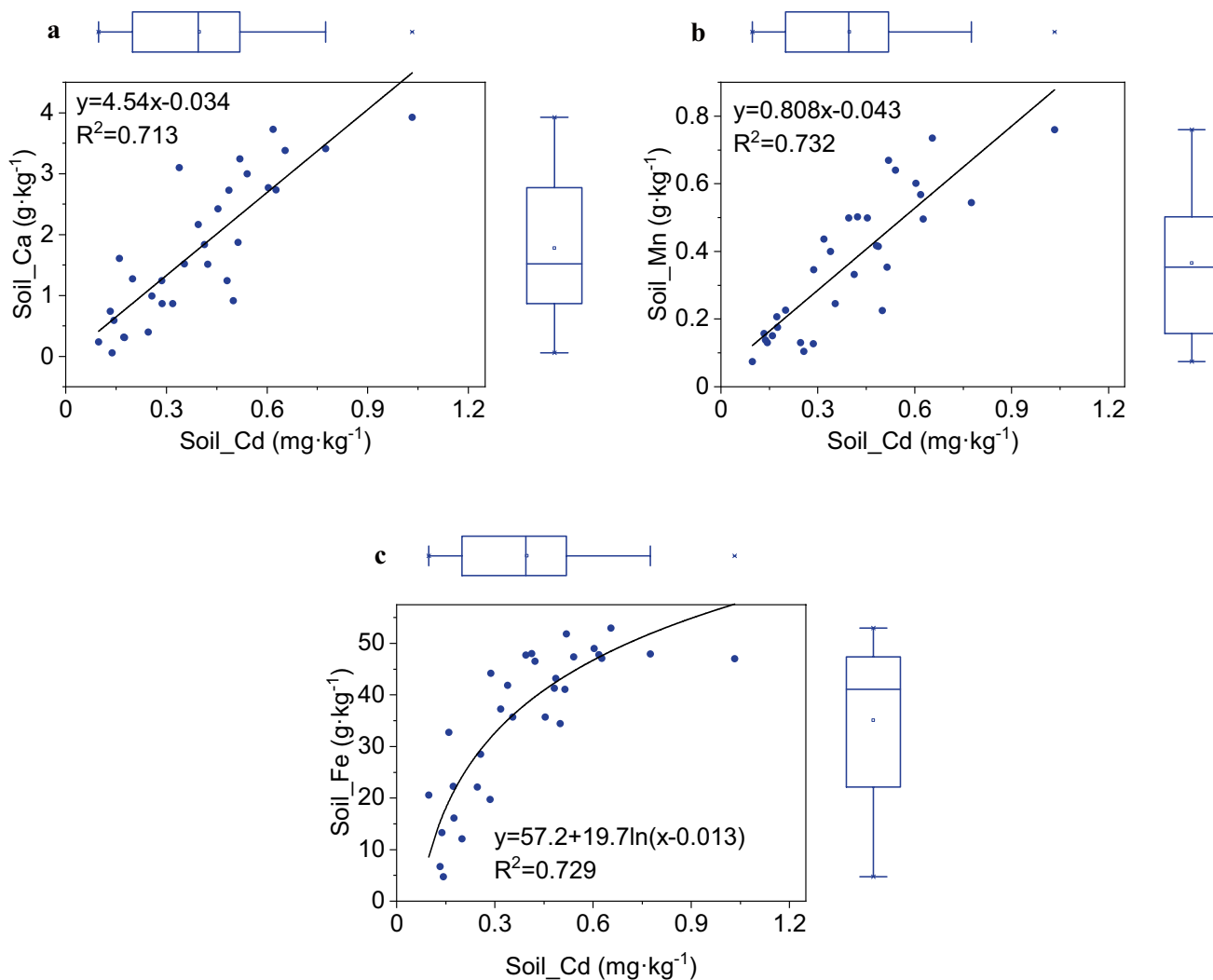
Fig. 2 Relationships between Soil_Cd and Soil_Ca (**a**); Soil_Cd and Soil_Mn (**b**); Soil_Cd and Soil_Fe (**c**)
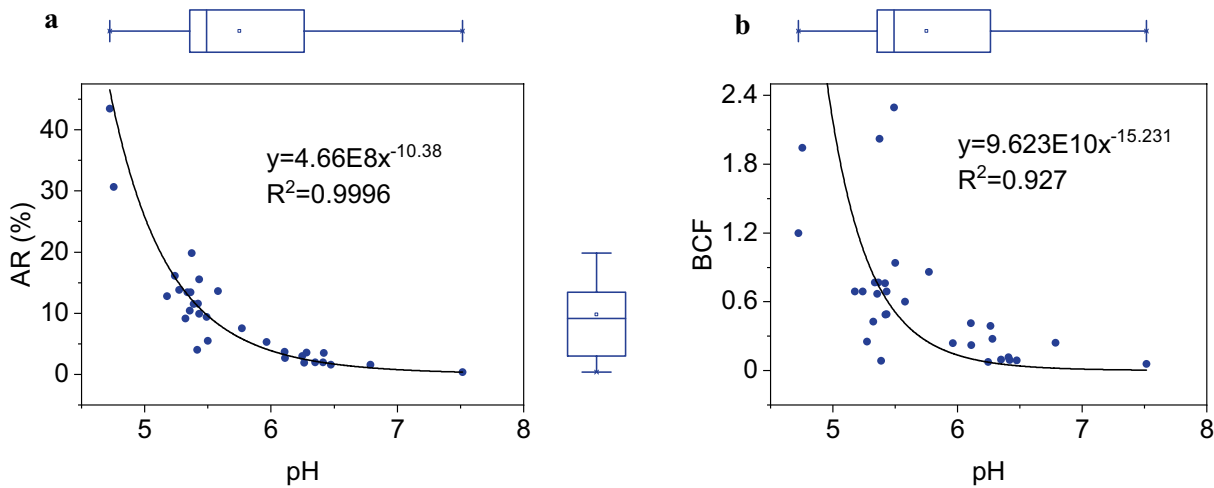

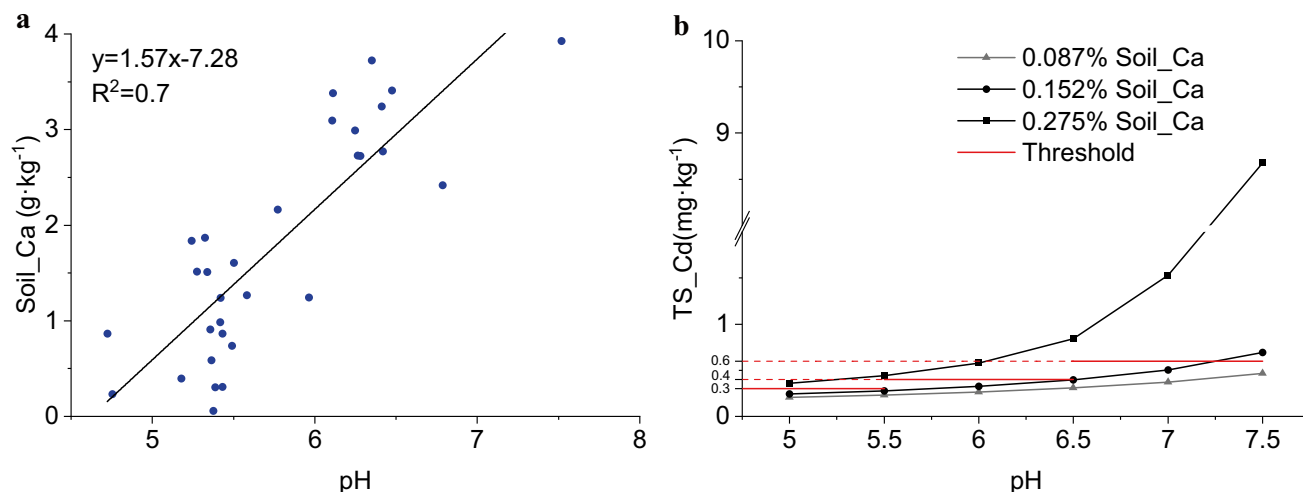**Fig. 3** Relationships between soil pH and AR (**a**) and BCF (**b**)

Fig. 4 a Correlations between pH and Soil_Ca. **b** Variations of TS_Cd at different soil pH and Ca contents. *Note* Soil_Ca = 0.087%, 0.152% and 0.275% respectively represented 25th, 50th and 75th per-centile of Soil_Ca; The red line represents the screening values of total Cd in soil at different pH (GB 15618 − 2018).

may represent water-dissolved and exchangeable Cd, but the release of carbonate-bound Cd and Fe–Mn oxide-bound Cd can be transformed to available Cd with the decrease of pH (Guo et al. 2019). Studies have shown that acid rain will aggravate the acidification of the soil, allowing more heavy metals to be resolved from the soil (Li et al. 2015; Moharami and Jalali 2015; Wang et al. 2009). In addition, it accelerates the rate of chemical weathering, which causes the heavy metals to be released faster from the rock (Zheng et al. 2017; Zhu et al. 2020).

Higher AR means more Ava_Cd in soils, leading to the accumulation of excessive Cd in plants. Similar to AR, the correlation between BCF and pH was also significantly negative ($R^2 > 0.9$) (Fig. 3b). This suggests that lower pH may activate Cd in soil and increase the risks of rice grain contamination. Our findings agree with previous studies, which have shown strong linear positive correlations between Grain_Cd and Ava_Cd or Soil_Cd (Römkens et al. 2009; Rodrigues et al. 2012; Wen et al. 2020). In contrast to pH, SOM has much weaker correlations with AR and BCF ($R^2 < 0.1$).

Soil_Ca had a significantly positive correlation with pH ($R^2 = 0.7$) (Fig. 4a). Based on the relationships among BCF, soil pH and Ca content, a linear model was constructed:

$$BCF = 20.229 − 0215pH − 0.216Soil\_Ca (R^2 = 0.5, RMSE = 0.439) \quad (3)$$

With this model, we could use soil pH and Ca to estimate Soil_Cd threshold values (TS_Cd) to keep Grain_Cd from exceeding 0.2 mg kg^{-1} (Chinese limit for rice grain Cd concentration, GB 2762 − 2017). At the same Soil_Ca level, TS_Cd increases with increasing pH (Fig. 4b). On the other hand, at the same pH level, decline of Soil_Ca

leads to lower TS_Cd. In this study, at 0.275% Soil_Ca, TS_Cd all exceeded the soil quality criteria for pH 5.5–7.5 (Fig. 4b), implying that risk of Cd pollution in rice grain was reduced. Higher pH may reduce the mobility of Cd in the calcareous soil (Paul-Olivier et al. 2013). Furthermore, Cd^{2+} and Ca^{2+} may compete for adsorption in the rhizosphere, thereby reducing the bioavailability of Cd (Yang et al. 2020). In other cases except for Soil_Ca = 0.152% and pH 7.5, predicted TS_Cd values were lower than the screening values of Chinese National Soil Quality Criteria (GB 15,618 − 2018) (Fig. 4b), further indicating important roles of soil pH and Ca in controlling rice grain Cd. In areas with low soil pH due to the decrease of soil Ca (such as 0.087% or 0.152% Soil_Ca), Cd bioavailability in soils and ecological risk of Grain_Cd increased. In comparison, under the same soil pH, the TS_Cd was larger (0.89–2.65 mg kg^{-1}) due to the higher content of Ca (50th Soil_Ca = 0.4%) in the upstream karst area (Wen et al. 2020).

In summary, soils of Doumen and Xinhui Districts demonstrated characteristics of HGB of transportation and deposition, which was the main reason for Soil_Cd higher than the level of natural background. Both Cd bioavailability and uptake by rice were significantly affected by soil pH and Ca content, which could also be used to predict threshold values of soil Cd to minimize the risk of Cd contamination in rice grain.

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