Cadmium Accumulation Risk in Vegetables and Rice in Southern China: Insights from Solid-Solution Partitioning and Plant Uptake Factor

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S Supporting Information

ABSTRACT: Solid-solution partitioning coefficient (K_d) and plant uptake factor (PUF) largely determine the solubility and mobility of soil Cd to food crops. A four-year regional investigation was conducted in contaminated vegetable and paddy fields of southern China to quantify the variability in K_d and PUF. The distributions of K_d and PUF characterizing transfers of Cd from soil to vegetable and rice are probabilistic in nature. Dynamics in soil pH and soil Zn greatly affected the variations of K_d . In addition to soil pH, soil organic matter had a major influence on PUF variations in vegetables. Heavy leaching of soil Mn caused a higher Cd accumulation in rice grain. Dietary ingestion of 85.5% of the locally produced vegetable and rice would have adverse health risks, with rice consumption contributing 97.2% of the risk. A probabilistic risk analysis based on derived transfer function reveals the amorphous Mn oxide content exerts a major influence on Cd accumulation in rice in pH conditions below 5.5. Risk estimation and field experiments show that to limit the Cd concentration in rice grains, soil management strategies should include improving the pH and soil Mn concentration to around 6.0 and 345 mg kg⁻¹, respectively. Our work illustrates that re-establishing a balance in trace elements in soils' labile pool provides an effective risk-based approach for safer crop practices.

KEYWORDS: solid-solution partitioning, plant uptake, rice, vegetable, cadmium

INTRODUCTION

Cadmium (Cd) is one of the most harmful and widespread contaminants in agricultural soil.^{1,2} Cd is readily taken up by crop plants and threatens human health through the food chain.³ Dietary food intake accounts for approximately 90% of the total Cd exposure,² and vegetables and rice are the biggest contributors to Cd exposure in the general nonsmoking population.^{4–6} Long-term consumption of Cd-contaminated vegetables and rice is associated with osteoporosis, kidney disease, and cardiovascular disease.^{7,8} China produces and consumes more vegetables and rice than any other country in the world.^{9,10} About 13 million hectares of the cultivated land of China is reported to be contaminated by Cd.¹¹ Therefore, an important and urgent task in China is to control the risks associated with Cd in crop plants.

Vegetable and rice plants take up Cd from its labile pool in soils.^{12,13} Solid-solution partitioning and plant uptake are important processes determining metal bioavailability, phytoavailability, and ecotoxicity.^{14–16} The solid-solution partitioning coefficient (K_d) is often used to estimate metal ion concentration or activity in soil and predict metal mobility as well as potential leaching losses.^{17,18} The potential transfer of trace metals from soil to plants is usually estimated by the dimensionless plant uptake factor (PUF) defined as the ratio of metal concentration in edible plant tissues to that in soil.¹⁹ Both K_d and PUF help normalize the differences caused by mineralogical and soil conditions, and thus standardize the risk assessment of trace metals in soil-crop systems.^{20,21} K_d and PUF are introduced in many studies to predict the potential

risk of toxic metals in cropland soil,²² inform soil protection guideline,²³ and assess the Cd intake risk.²⁴ Simple generic values of K_d and PUF are widely used in risk assessment models such as the Contaminated Land Exposure Assessment Model in the U.K.,²⁵ the Csoil Model in The Netherlands,²⁶ and the Cadmium Accumulation Model in China.²⁷ However, these two parameters are not constants but vary widely with different environmental factors.^{14,19} Significant variables contributing to the variability of K_d and PUF are soil pH, soil organic matter, cation exchange capacity, texture, Fe/Mn oxides, and crop plant species.^{5,28}

Predictive K_d and PUF models factoring in soil pH have been developed in recent years.^{16,23} The limitation of these studies is that the transfer functions are not universal and cannot be generally used to accurately assess potential risk of Cd in agricultural systems. Lim et al.,¹⁸ Sauvé et al.,²⁸ and Groenenberg et al.²⁹ compared their derived models with experimental results and indicated that literature-derived functions underestimate the site-specific environmental factors. The processes of soil Cd accumulation and crop uptake are dynamic and complex,^{12,30} but K_d and PUF are seldom parametrized accordingly. In addition, most studies were conducted over only one year and were carried out on spike metals or potted experiments having a narrow range of soil

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Figure 1. Probability distribution of (a): K_d in vegetable and paddy fields; and (b) the PUF of vegetable and rice from the study area and other studies. K_d and PUF data are fitted by a log-normal distribution function. The K_d data in Nanjing and California from Chen et al.²¹ and Luo et al.²² The PUF data in China and U.S.A. from Chen et al.²¹ and Zhang et al.³⁶

compositions.^{17,23} The limited field data restrict the use of these K_d and PUF models in risk assessments.²⁵ Many national environmental agencies recommend developing systematic methods to characterize K_d and PUF to determine site-specific risk and ultimately human exposure,^{21,22,24} but such detailed comprehensive studies are limited.

The prefecture of Youxian is a major regional crop producer in southern China (Figure S1 in the Supporting Information) and is known nationwide as a “Cd-tainted rice” region.¹³ On the basis of a four-year regional investigation and field trial in vegetable and paddy fields of this area, we aimed (1) to characterize K_d and PUF in probabilistic terms; (2) to identify the major factors influencing K_d and PUF; and (3) to provide recommendations toward a more risk-based perspective for the safer production of vegetables and rice.

MATERIALS AND METHODS

Survey and Sampling. A total of 683 paired soil-crop sites were selected throughout the Youxian prefecture (113.32°E long., 27.01°N lat.), including 478 vegetable field sites and 205 paddy field sites. At each site, the types of crop cultivars and growth conditions were investigated and recorded. Five major consumed leafy-type vegetables in the study area were collected, comprising bokchoy (*Brassica rape* var. *chinensis*), Chinese cabbage (*Brassica pekinensis* L.), mustard (*Brassica juncea* L.), lettuce (*Lactuca sativa* L.), and red cabbage (*Brassica campestris* subsp. *chinensis* var. *purpuria*). Rice samples belonged to the late *indica* cultivars. Topsoil samples (0–20 cm) were collected from the site of each crop plant harvest. Detailed information on samplings is available in Table S1 in the Supporting Information (SI).

The amount of crop residue returning to the soil was measured in the fields following each year’s harvest using the methods described in Wang et al.³¹ Meteorological data and agronomic information including farmland cultivation, management, irrigation, fertilization and the main agricultural inputs and outputs were recorded and are listed in Tables S2 and S3. The consumption ratios of the vegetables (46.4 ± 23.6 g DW d^{−1}) and rice (258 ± 78.7 g DW d^{−1}) in the study area were obtained using a standardized questionnaire survey ($n = 671$, Table S4) throughout the study area. The body weights of adults (58 ± 9.1 kg capita) were obtained from a health survey ($n = 3442$) conducted by the Youxian health agency (Table S4).

Chemical Analyses. Samples of soil, vegetable, and rice were prepared according to the procedure described in Wang et al.¹³ and Yang et al.³² The bulk density of soil was measured with the core cutter method.³¹ The soil pH and electrical conductivity were measured in 1:2.5 and 1:5 (w/v) soil and water suspension, respectively. The contents of soil organic matter ($K_2Cr_2O_7$ – H_2SO_4 ,

oil-bath-heating), clay (hydrometer method), cation exchange capacity (1 mol NH_4OAc buffered at pH 7.0), total C and N (dry combustion method), amorphous Fe, and Mn oxide ($(NH_4)_2C_2O_4$ – $H_2C_2O_4$ extraction) were analyzed according to routine analytical methods of agricultural chemistry in soil.³³ The solubility and speciation of Cd were determined using 1:2 (w/v) soil extracts with 10 M KNO_3 to eliminate the influences of other salts on the total ionic strength of the solution.²⁸ The detailed procedure is described in Luo et al.²²

The crop samples were digested with concentrated HNO_3 – $HClO_4$, whereas soil was digested with a mixture of HCl – HNO_3 – HF – $HClO_4$ solution.^{13,33} Concentrations of Cd and Zn were determined by GFAAS (ZEEnit700, Analytik Jena, Germany).³⁴ Concentration of Fe and Mn were determined by ICP-OES (DV4300, PerkinElmer, Norwalk, U.S.A.).³⁴ Basic information on determined physicochemical properties in the vegetable and paddy fields included in this study is available in the Table S5.

Quality Assurance. Sample blanks and standard reference materials (GBW10014 for vegetables, GBW10045 for Hunan rice, and GBW07405 for soils) were included in every batch of the analyses.³⁵ The recovery ratios of standards for Cd and Zn ranged from 82.4% to 118% and 79.5% to 119% for GBW10014, 93.1% to 108% and 83.8% to 121% for GBW10045, and 92.1% to 110%, and 83.7% to 118% for GBW07405, respectively.

Statistical Analyses. One way analysis of variance (ANOVA) was conducted to evaluate the differences in vegetable and paddy fields, in which significant effects were compared using the Turkey’s test ($p < 0.05$). Spearman correlation analysis (two-tailed) and stepwise multiple linear regression analysis were conducted using the Genstat 17.0. The uncertainty in the risk assessments was estimated using the Monte Carlo simulation method, obtained following 10 000 iterations using the Matlab 14.0a.

RESULTS AND DISCUSSION

Characterization of K_d and PUF. As shown in Figure 1, K_d values ranged from 3.24 to 5,145 L kg^{−1}, with a geometric mean value of 35.5 L kg^{−1}. The range of K_d values was within the range reported by Sauvé et al.²⁸ (0.44–192 000 L kg^{−1}), but comparatively narrower. K_d values in paddy fields (geometric mean $K_d = 29.5$ L kg^{−1}) were significantly lower than that in vegetables fields (geometric mean $K_d = 38.4$ L kg^{−1}), suggesting that Cd in solution phase is proportionately higher in paddy soils, thus increasing the accumulation risk for rice crops. The PUF value averaged 1.52 for rice fields, nearly 10 times that of vegetable fields (0.15) (Table S5). About 0.2% and 62% of vegetable and rice fields had PUF values above 1. These results demonstrate that Cd is effectively transferred from soil to rice grains.

Figure 2. Relationship between soil pH and K_d in (a) vegetable and (b) paddy field.

Table 1. Derived Transfer Functions for K_d and PUF in Vegetable and Paddy Field

no. of equations	field	regression model	model validation			
			<i>n</i>	R^2	RMSE	<i>p</i>
1	vegetable	$\log[K_d] = -3.17 + 0.74 \text{ pH} + 0.27 \log[\text{Zn}] + 0.29 \log[\text{SOM}]$	478	0.69	0.41	<0.001
2	rice	$\log[K_d] = -5.41 + 0.83 \text{ pH} + 1.3 \log[\text{Zn}]$	205	0.81	0.19	<0.001
3	vegetable	$\log[\text{PUF}] = 1.08 - 0.25 \text{ pH} - 0.54 \log[\text{SOM}]$	478	0.62	0.19	<0.001
4	rice	$\log[\text{PUF}] = 2.04 - 0.23 \text{ pH} - 0.43 \log[\text{Mn}_{\text{ox}}]$	205	0.37	0.26	<0.001
5	rice	$\log[\text{Cd}_{\text{rice}}] = 1.62 - 0.22 \text{ pH} + 0.26 \log[\text{Cd}_{\text{soil}}] - 0.41 \log[\text{Mn}_{\text{ox}}]$	205	0.42	0.23	<0.001

Figure 1 also illustrates that the distribution of K_d and PUF in the Youxian prefecture and data from other studies are better matched by a probabilistic distribution function.^{21,36} K_d values range approximately over 3 orders of magnitude, and are lower than reported K_d values in Nanjing and California (Figure 1a), suggesting that fields in the studied region have generally poor Cd retention capacity. These results further illustrate the seriousness of the Cd contamination situation in the cropland soils of the Youxian prefecture.

The PUF values showed a 41-fold and 70-fold variation in vegetable and rice fields (Figure 1b), respectively. In comparison with the PUF values throughout the cropland soils of China and California, the PUF of rice fields in our study is much higher, while PUF of vegetable fields in this region is much smaller, suggesting a potential risk for rice cultivation in the study area. Correlation analyses showed a weak relationship between total Cd in soils and crop plants. Among uncontaminated soil (soil Cd < 0.3 mg kg⁻¹),³⁷ 67.1% (102 of 152) of vegetable fields had low levels of PUF (lower than their averaged value, 0.15), and 62.2% (46 of 74) of paddy fields had low levels of PUF (lower than their averaged value, 1.52). These results indicate that soil Cd alone is generally a poor predictor for Cd accumulation in crop plants.

In general, the great site-to-site variations of K_d and PUF indicate a complicated relationship between Cd concentration in soil, soil solution, and crop plants and environmental factors, thus making risk assessment and management more challenging. Although the use of representative K_d and PUF values in relevant works may be similar,^{24,26,28} the probability risk interpretations are quite different. Results indicate that characterizing K_d and PUF in probabilistic terms is necessary for a consistent risk assessment.

Relationships Between K_d and Soil Factors. The bioavailability of Cd in agricultural soil is governed by a range of soil factors.^{6,12} Values of K_d showed a curvilinear increase with pH over the range 3.4–7.84 (Figure 2). Soil pH alone accounted for 58% and 71% of the variability in vegetable

fields and paddy fields, respectively, suggesting that Cd in paddy fields is more sensitive to the influence of soil pH than in vegetable fields.

A pH value of 5.5 is the acidification threshold of soils in southern China.³⁷ The K_d values in both vegetable and paddy soils are divided into two groups depending on this pH threshold, as shown in Figure 2. In the acidic soil group (pH < 5.5), 56.1% (268 of 478) of vegetable fields had low levels of K_d (lower than their geometric mean, 38.4 L kg⁻¹), and 56.1% of paddy fields (115 of 205) had low levels of K_d (lower than their geometric mean, 29.5 L kg⁻¹). Soil acidification increases deprotonation of the soil surface and therefore reduces the adsorption capacity and the holding capacity of Cd in agricultural soils.^{9,17} Soil pH in sampled soils averaged 5.3, and 74.4% of fields (508 of 683) belonged to the acidic soil group (pH < 5.5). The strong acidification of soils in study area implies a lower retention capacity of cationic Cd and thus uptake by crop plants.

Stepwise multiple linear regression was used to describe the relationship between analyzed factors based on the extended Freundlich-type function,²⁹ as shown in Table 1. In addition to the pH, soil Zn greatly affected the variations of K_d in both soil types (eqs 1 and 2, Table 1), since Zn and Cd in the available metal pool have similar affinity for sorption sites.^{15,29} Soil organic matter (SOM) readily binds Cd cations and can form strong complexes with them and thus reduces the bioavailability of the metal,¹⁶ and this effect was significant in vegetable soils (eq 1, Table 1). In both soil types, cation-exchange capacity (CEC), clay, amorphous Fe oxide (Fe_{ox}), and amorphous Mn oxide (Mn_{ox}), and nitrogenous fertilizer input showed a correlation with pH, SOM and Zn ($r = 0.106^* - 0.395^{**}$), suggesting that these factors may influence Cd bioavailability indirectly.

In the study area, paddy fields were ploughed deeply once or twice annually, whereas vegetable soils were ploughed more frequently (the mode of cultivation varied between 3 deep ploughings and 15 shallow ploughings) (Table S3). Frequent

Figure 3. Influence of (a) soil pH and Mn_{ox} on rice PUF (the bigger the circle, the larger the PUF value); (b) Mn fertilizer (MnSO₄) on the PUF of rice grain and rice root (the low and high Mn treat represent the rates of 75 and 375 kg ha⁻¹, respectively; the low Mn treat increased the soil Mn content from 268 to 294 mg kg⁻¹ and from 250 to 284 mg kg⁻¹ for early rice and late rice crops in 2015, and the high Mn treat increased the soil Mn content from 254 to 365 mg kg⁻¹ and from 252 to 595 mg kg⁻¹ for middle rice and late rice crops in 2016, respectively; bars with different letters indicate significant differences ($p < 0.05$) between Mn treatments).

ploughings cause a strong disturbance of the surface soil profile (0–20 cm), destroy soil aggregates, improve the soil aeration porosity, and speed up the decomposition and mineralization of SOM.^{10,31} Fields ploughed three times a year or more for vegetable production required more fertilizer input. The application of nitrogenous fertilizer in the vegetable and paddy fields in this study reached 332 and 140 kg ha⁻¹, respectively, significantly higher than applications of phosphorus and potassium fertilizer (Table S3). The negative correlation between nitrogenous fertilizer input and soil pH ($r = -0.366^*$) and SOM ($r = -0.219^*$) in vegetable fields shows that excessive fertilizer application may lead to soil acidification and a decline in SOM owing to nitrification and physiological acidity.^{9,11} In addition, vegetable field practices led to drought conditions during the whole tillage stage, while paddy fields alternated between dry and wet conditions. Aerobic and warmer conditions further led to decreases in Fe_{ox} and Mn_{ox} in vegetable fields (Table S5). Accordingly, the decreases of SOM, CEC, Fe_{ox}, and Mn_{ox} resulted in a higher solubility of Cd²⁺ in vegetable fields compared to paddy fields. Other studies in Hunan,¹⁰ Guangdong,³¹ and Jiangsu³⁸ found similar decreased soil fertility conditions in vegetable fields compared with paddy fields.

Relationships Between PUF and Soil Factors. The derived transfer functions revealed that in addition to soil pH, SOM had a major influence on PUF variation in vegetable fields, and Mn_{ox} is the principal control factor of PUF in rice field (eqs 3 and 4, Table 1). In the acidic soil group (pH < 5.5), the PUF averaged 0.2 and 1.6 for vegetable and rice fields, respectively, and was significantly higher than the PUF in fields with pH values above 5.5. In particular, the low K_d values (lower than their geometric mean value) were mainly located in sites with soil pH < 5.5 (Figure 2). These results suggest that soil acidification increased the Cd availability and thus uptake by crop plants.

SOM was closely correlated with PUF in vegetable fields ($r = -0.362^{**}$) (Table S6). When the SOM content was below 10 g kg⁻¹, 63% of the vegetable fields had a PUF greater than their mean value (0.15). This ratio significantly decreased to 17.2% when SOM content in vegetable soil increased to 30 g kg⁻¹. The relationship between SOM and rice PUF is relatively poor ($r = 0.053$). The root biomass and plant residue amount of vegetables was only 33.7% of that in rice, which resulted in a

significantly lower C/N ratio in vegetable fields (10.4) compared to paddy fields (12.4) (Table S5). Low C/N in vegetable fields shows an inhibitory effect on microorganism activity, and decreases microbial biomass and metabolites.³⁸ This could partially explain the lower SOM in vegetable fields (20 g kg⁻¹) compared to paddy fields (39.6 g kg⁻¹) (Table S5), and the significant influence of SOM on Cd accumulation in vegetables.

A Mn transporter (OsNRAMP5) has recently been proposed as the major Cd uptake pathway in rice.^{7,30} As shown in Figure 3a, PUF values of paddy soils are separated clearly into two groups by the Mn_{ox} content of 82 mg kg⁻¹. About 83.8% of rice fields with a PUF above 1 were distributed in sites with soil Mn_{ox} below 82 mg kg⁻¹. The PUF level in this low-Mn_{ox} group averaged 2.0, significantly higher than in the high-Mn_{ox} group (average 1.03). Our investigation also showed that Cd uptake by rice can be significantly inhibited by soil Mn_{ox}, indicated by the strong negative correlation between soil Mn_{ox} and Cd accumulation in rice roots ($r = -0.389^{**}$) and rice grain ($r = -0.499^{**}$). Our field experiments over four rice growing seasons demonstrate that Mn application is effective in reducing Cd uptake in rice, as the PUF of rice roots and rice grains decreased by 27.2% and 44.5%, respectively, as shown in Figure 3b.

The average and median value of Mn concentration in paddy soils were 248 and 209 mg kg⁻¹, respectively, far below the soil background value (459 mg kg⁻¹).³⁹ The high temperature (Table S2) and drainage of paddy fields in the mature stage result in aerobic conditions that enhance the soil acidity and Mn²⁺ oxidation.^{6,8,15} This in turn aggravates the loss of Mn due to drainage in paddy fields, and consequently weakens the effect of Mn in suppressing Cd transfer from soil to rice grain.

The average concentration of Zn in the vegetable and paddy field was 111 and 99.5 mg kg⁻¹, respectively (Table S5), and slightly higher than the soil background value of 94.5 mg kg⁻¹.³⁹ The relationship between soil Zn and vegetable Cd was poor ($r = 0.064$). However, a negative correlation ($r = -0.399^{**}$) between Zn and Cd accumulation in vegetable soils was found in areas that had a Zn:Cd ratio around 50:1. In the paddy fields, Zn had little influence on Cd accumulation ($r = 0.062$). These areas suffer from strong acidification and serious Cd contamination, which cause a dysfunction in the soil-crop

Figure 4. Predicted Cd concentrations in rice (mg DW kg^{-1}) grown in a combination of different pH, soil Mn_{ox} and soil Cd of (a) low contamination (0.3 mg kg^{-1}) and (b) heavy contamination (1.5 mg kg^{-1}). The white and grey circles from left to right indicate the predicted Cd concentration in rice harvested from low Mn_{ox} (82 mg kg^{-1}) and high Mn_{ox} (132 mg kg^{-1}) soil with pH of 5.0, 5.5, and 6.0, respectively.

ecosystem and alter the normal ratios of Zn:Cd (100:1, suggested by Chaney³⁰).

Risk Prediction. The daily intakes (DI) of Cd through consumption of vegetables and rice are estimated using the health risk equation and Monte Carlo simulation (details are given in the SI). DI averaged 0.06 and $2.1 \mu\text{g BW kg}^{-1} \text{ day}^{-1}$ for vegetable and rice, respectively (Figure S2). About 85.5% of the adult population living in affected areas had a daily Cd intake risk above the toxic value recommended by JECFA ($0.8 \mu\text{g BW kg}^{-1} \text{ day}^{-1}$),⁴ with rice consumption contributing 97.2% of the risk (Figure S2). A ratio of Cd to Zn in food crops below 0.015 is reported to effectively protect from Cd-induced health impacts.^{1,3} About 98.3% and 23.9% of vegetables and rice samples were within this safe ratio, respectively. Considering the greater risk posed by rice consumption, the factors governing Cd accumulation in rice are more important than those in vegetables in terms of practical farmland management.

A linear relationship describing Cd transfer from soil to rice grain was also established using the stepwise multiple linear regression method, as shown in eq 5 in Table 1. On the basis of the Monte Carlo simulation method, the derived transfer function (eq 5) can be used to predict the likely content of Cd in rice grains in different soil conditions (for the parameters of pH and Mn_{ox} in eq 5, values were randomly drawn from their measured distributions²⁴). As expected, the estimated Cd concentration in rice increased with soil Cd concentrations and decreased with soil Mn_{ox} content and soil pH (Figure 4). Cropping rice in low contamination area (soil Cd = 0.3 mg kg^{-1}),³⁷ caused a 94.5% and 43.3% likelihood of Cd to accumulate above the China food standard limit of $0.2 \text{ mg DW kg}^{-1}$,⁴⁰ and the WHO limit of $0.4 \text{ mg DW kg}^{-1}$,⁴¹ respectively; while this risk was significantly increased to 99.4% and 81.6%, respectively, in seriously contaminated soils (soil Cd = 1.5 mg kg^{-1}).³⁷

As illustrated in Figure 4a, under uncontaminated soil conditions (soil Cd < 0.3 mg kg^{-1}),³⁷ and low levels of Mn_{ox} (82 mg kg^{-1}), rice grown in strong acidic soil (pH = 5.0), acidic soil (pH = 5.5), and near-neutral soil (pH = 6.0)³⁷ resulted in a risk of 100%, 78.7%, and 36.7%, respectively, of producing Cd-tainted rice ($>0.4 \text{ mg DW kg}^{-1}$). This risk significantly decreased to 82%, 39.5%, and 18.8%, respectively, when soil

Mn_{ox} increased to 132 mg kg^{-1} (Figure 4a). This result indicates the influence of Mn_{ox} and pH on Cd accumulation in rice is interactive and dynamic. Mn_{ox} content controlled the variations of rice Cd when Mn_{ox} was less than 82 mg kg^{-1} , especially in pH below 5.5.

Field experiments indicate that in improved soil conditions, with a pH of ~ 6.0 and a Mn_{ox} of $\sim 132 \text{ mg kg}^{-1}$, the risk of rice Cd exceeding $0.2 \text{ mg DW kg}^{-1}$ significantly decreased from 100% to 33.3% (Figure S3), agreeing with our estimation (Figure 4a). To maintain acceptable Cd concentrations in rice grains ($<0.2 \text{ mg DW kg}^{-1}$),⁴⁰ soil management strategies should aim to improve soil pH to ~ 6.0 and soil Mn to $\sim 345 \text{ mg kg}^{-1}$ (roughly corresponding to $132 \text{ mg kg}^{-1} \text{ Mn}_{\text{ox}}$, Figure S4).

At present, the continuous acidification of paddy soils raises concerns in the government and farming communities.^{11,42} To improve the acidic condition of cropland soil, large applications of lime and biochar have been conducted in many areas of southern China.^{9,42} However, the use of these materials may result in a serious loss of soil trace elements, especially in paddy soils with a low level of Mn. Rebuilding the element balance in cropland soils is more likely to provide an effective risk-based approach for safer crop production, rather than enforcing a strict ban on the usage of discharging Cd-contaminated effluents on soils, or removing the Cd from contaminated soils via engineering projects. Characterizing the K_d and PUF and their relationships with site-specific factors in probabilistic terms provide different tools to assess soil contamination and are useful in effective risk management.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.7b01931.

Details on Cd intake risk estimation (eqs S1–S3), regional investigation (Tables S1–S5, Figure S1) and the relationship between environmental factors and K_d and PUF from vegetable and paddy fields (Tables S6, Figures S2–S4) (PDF)

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Notes

The authors declare no competing financial interest.

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