Research paper

Application of DGT/DIFS to assess bioavailable Cd to maize and its release in agricultural soils

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ABSTRACT

Tianjin, as an important maize production region in China, has a long history of sewage irrigation resulting in the soil cadmium (Cd) contamination. In this study, single extractions of $CaCl_2$ and HNO_3, BCR sequential extraction and the diffusive gradients in thin films technique (DGT) were used to measure the bioavailable Cd content in soils. The Cd content in soil samples all exceeded the background values, with 14.3% and 33.3% of sites in the Baodi District (BDD) and Jinghai District (JHD) exceeding the risk control values, respectively. The average content of Cd in maize samples is lower than the pollution control values, which may be related to the higher pH (8.53) and organic matter (OM) content (15.01 g kg^{-1}) in soils. Bioavailable Cd measured by DGT correlated well with Cd in maize grains (R^2 =0.92). The DGT and DIFS model predicted the metals release from the agricultural lands, the total concentration of Cd in soil was relatively low, but the labile Cd in the soils has adequate metal release capability. This study shows that DGT is efficient in predicting Cd accumulation in grains from contaminated soils.

1. Introduction

Cd is a non-essential element for humans that widely exists in the environment. The toxicity and non-biodegradability of Cd pose severe threats to human health (Maity et al., 2018). Generally, anthropogenic activities can accelerate the release of metals into soils through industrialization, urbanization, mining activities, and irrigation of associated raw wastewaters (Rehman et al., 2018). Millions of hectares of agricultural land are seriously enriched by Cd in China (Bashir et al., 2018). A previous soil pollution census reported that among the seven major toxic metals and metalloids, Cd exceeded the Chinese national standard at the highest rate (7%) (Wang et al., 2019a, 2019b). One of the most important sources of contamination in Chinese farmlands is sewage irrigation, which has discharged more than 125 t of Cd to soils over the past six decades (Shi et al., 2019). Importantly, the quality and safety of agricultural soils are directly correlated to food security, and Cd can be easily enriched through the food chain (Rehman et al., 2017). Hence, increasing attention has been paid to the health risks originating from exposure to Cd-polluted soils.

Due to its high mobility, Cd can easily enter plant tissues, therefore, its accumulation in agricultural land as a result of sewage irrigation often shows a close relationship with the contamination of crops (Rizwan et al., 2016). Existing national standards usually use the total amount of metals as the parameter of measurement, such as Soil environmental quality Risk control standard for soil contamination of agricultural land (GB 15618-2018). But the bioavailability of different pollutants to crops are not taken into account in these standards. Traditional model for assessing the biological effectiveness of Cd is the free ion activity model (Almas et al., 2006), while traditional methods include chemical extraction (Ngo et al., 2016) and the isotope dilution method (Shetaya et al., 2018). Considering the absorption by plants at the boundary between soil and roots, the equilibrium-based approaches mentioned above (Chomchoei et al., 2002) are able to identify metal species that may be readily taken up by plants. But they cannot accurately simulate the uptake of trace metals by crops.

To investigate the dynamic release of heavy metals in soil, the diffusive gradients in thin films technique (DGT) has been developed as a passive sampling tool based on diffusive and binding phases (Davison

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and Zhang, 1994). Fick's first law of diffusion is the theoretical basis of the DGT. During the development of DGT, there has been a lot of work around selective binding phases, these studies have focused on the toxic elemental compounds. Pescim et al. (2012) used agarose gel immobilized brewer's yeast as a DGT-binding phase for the determination of Pb in both river and seawater. Tafurt-Cardona et al. (2015) used agarose gel-fixed brewer's yeast as the binding phase to selectively determine methylmercury in river water in situ. Labile metals are adsorbed by the binding layer, thus the equilibrium at the soil-DGT interface breaks, meaning that the DGT technique can determine not only metals in the liquid phase but also the fraction of resupply from soils after labile metals have been exhausted (Zhang et al., 2018). DGT has been a reliable means of assessing metal bioavailability, showing stable performance when mimicking concentration changes at the root-soil and pore-solid interfaces (Perez and Anderson, 2009; Dai et al., 2017; Gu et al., 2017). The studies conclude that DGT is more reliable than general methods for predicting Cd concentrations in ryegrass, wheat and earthworms (Gu et al., 2017; Perez and Anderson, 2009; Song et al., 2015). DGT is also more accurate at predicting plant available Se in natural and polluted soils (Wang et al., 2019a, 2019b). As known, the dynamic release of solid-phase metals in soil is closely related to plant adsorption. Therefore, the establishment of a trace metal mobility model has significance for predicting potential soil and crop risks. Another application of the DGT technique is the assessment of the dynamic release of trace metals, having proven to be reliable in simulating dynamic diffusion (Ernstberger et al., 2002). More useful information about the adsorption kinetics of soil particles has also been provided within the DGT-induced sediment flux (DIFS) model established (Harper et al., 1998, 2000; Xu et al., 2019). Since metal complexes can also be labile and the DIFS model does not consider any metal complexes present in the soil solution, in this work we neglect any complexes present in the soil solution.

There are thousands of hectares of land that have been irrigated with industrial and municipal wastewater for nearly 40 years in Tianjin, China (Liu et al., 2005). This is primarily due to the shortage of water resources in this region (Feng and Liu, 2006), and rapid industrialization and urbanization (Sun et al., 2018). Previous studies have revealed that the major pollutant metal in this region is Cd, and the ecological risks associated with the ingestion of fish, vegetables and wheat have been assessed (Meng et al., 2016; Wang et al., 2005, 2012). As a food crop widely planted in Tianjin, maize, which accounts for approximately 66% of the grain production croplands (Tianjin Municipal Bureau of Statistics & Survey office of National Bureau of Statistics in Tianjin, 2013), plays an important role in the livelihoods of local people, however there are few studies on the bioavailability of Cd to maize in Tianjin. Hence, the aims of this study were to investigate whether traditional chemical extraction and DGT techniques can predict the bioavailable Cd in maize.

2. Materials and methods

2.1. Site description and sample preparation

Wuqing District (WQD), Baodi District (BDD), Ninghe District (NHD), and Jinghai District (JHD) are the major maize production regions in Tianjin, accounting for 66% of maize growing area and 70% of the yield (Tianjin Municipal Bureau of Statistics & Survey office of National Bureau of Statistics in Tianjin, 2019). Most of the agricultural land is distributed in the largest 'northern sub-area' of the three districts with a long history of sewage irrigation over 45 years (Meng et al., 2016). Thus, based on the distribution of wastewater irrigation land and sizes of maize production regions (Fig. 1) 35 maize and corresponding surface topsoil samples were collected during the annual harvest period (September to October) in 2018. The GPS coordinates of the fields are shown in Table S1. The soil samples were obtained from the root zone (0–20 cm depths), which were air-dried and screened using a 150-μm nylon sieve. The grains of maize were washed with ultrapure water and
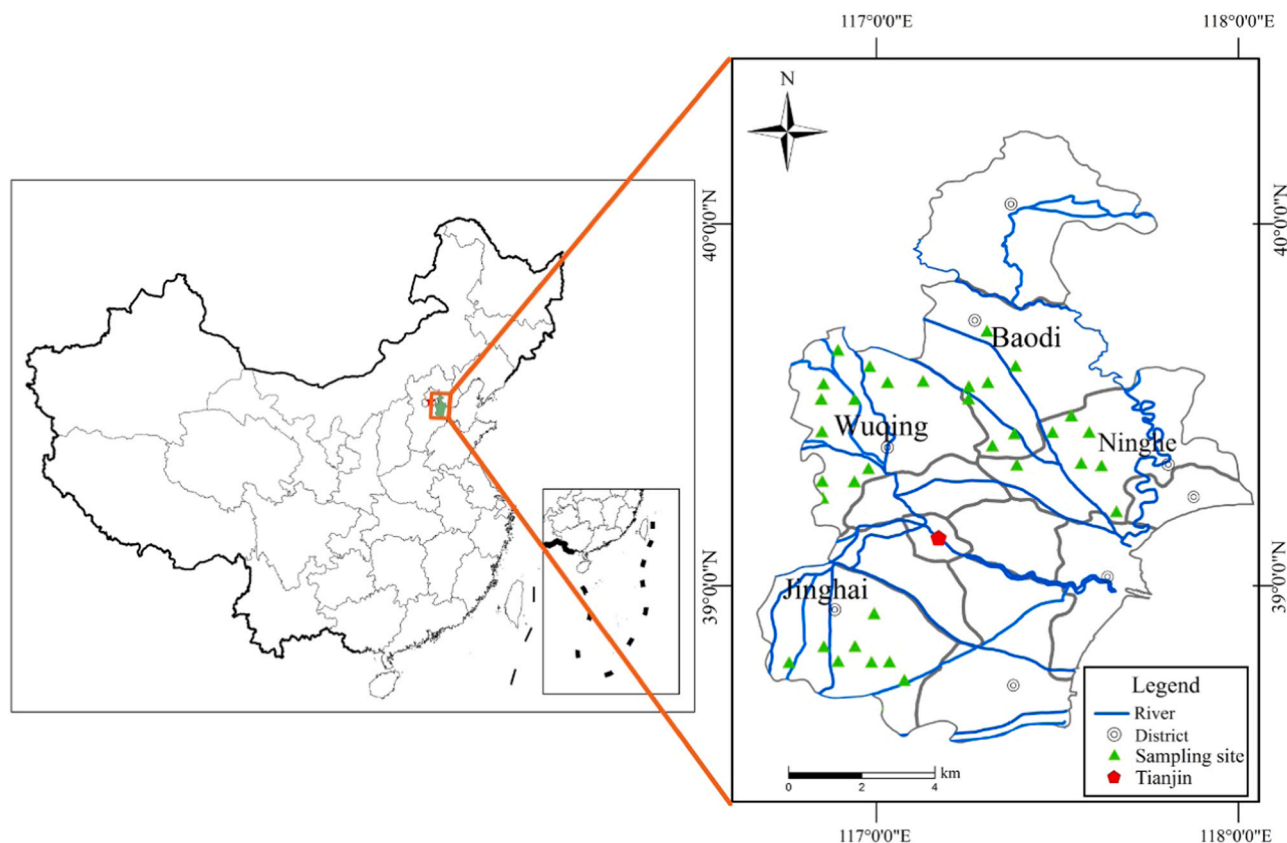

Fig. 1. Sampling sites in research districts.

dried to a constant weight at 80 ℃. After cooling, the grains were ground into fine powder and kept in plastic bags under dry condition.

2.2. Sample analysis

2.2.1. Determination of soil sample properties

The total concentration of Cd in the soil and maize samples was measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7900) after digestion with a combined acid solution (Rizwan et al., 2016). Briefly, 0.5 g of soil sample was put into a 50-mL test tube to which approximately 10 mL of HNO_3 (14.5 mol/L) and 4 mL of HF (22.5 mol/L) were added for a period of 12 h. The sample was digested at 120 ℃ for 2 h and 150 ℃ for 1 h, and then the temperature was increased to 170 ℃ to evaporate the acid until the volume of solutions approached 1 mL. For maize samples, 10 mL of HNO_3 (14.5 mol/L) and 2.5 mL of $HClO_4$ (12.3 mol/L) were added into 0.5 g grain powder followed by the same digestion procedure as soil samples. The 1 mL residual solution was diluted with ultrapure water to 50 mL and kept overnight. The supernatant in the test tube was filtered through a 0.45-μm polyethersulfone (PES) membrane before ICP-MS analysis.

After 5 g of soil and 25 g of deionized water were thoroughly mixed and settled, pH was determined using a pH meter (Mettler Toledo, Switzerland) (Wen et al., 2009). Soil organic matter (OM) was determined following a procedure developed by Walkley and Black (1934). Cation exchange capacity (CEC) was measured using the NaOAc-N-H_4OAc method (Dai et al., 2017). The maximum water holding capacity (MWHC) of the samples was calculated as the ratio of the water content of saturated soil to the dry soil weight (Gao et al., 2015). In this test, the soil was first wetted with ultrapure water to 60% MWHC, which is the ratio of water to soil that remains in the soil after release by gravity, and kept under sealed conditions at 23 ℃ for 2 days, then ultrapure water was added to 100% MWHC at the same temperature.

2.2.2. Single and sequential extractions

Based on the characteristics of the saline-alkali soils in Tianjin, two types of single-step extractions were carried out using 0.01 mol/L $CaCl_2$ and 0.43 mol/L HNO_3, respectively (Houba et al., 1992; Novozamsky et al., 1993).

The modified European Community Bureau of Reference (BCR) sequential extraction method was employed to analyze the Cd species in soil samples (Rauret et al., 2001). Briefly, the acid-exchangeable Cd (F1), reducible Cd (F2), and oxidizable Cd (F3) were extracted from soil samples sequentially using acetic acid, hydroxylamine hydrochloride (pH=1.5), and hydrogen peroxide/ammonium acetate (pH=2), sequentially. After extraction, the residual fraction was washed with ultrapure water and dried to constant weight prior to determining residual Cd (F4) using the method described in Section 2.2.1.

Mobility factor (MF) was used to characterize the relative mobility of metals (Kashem et al., 2007). Generally, MF is calculated as the ratio of F1 to the total concentration, which represents the fraction of metal easily desorbed from soil particles, and is thought to reflect the biological effectiveness of metals in soil (Salbu and Krekling, 1998; Nafiu et al., 2012).

2.3. DGT deployment

The assembled Chelex100-based DGT device was purchased from Easysensor Ltd. (www.easysensor.net). This device consists of a polyvinylidene difluoride (PVDF) membrane (0.10 mm), an agarose diffusive layer (0.80 mm), and a chelex-100 binding layer. Thirty g soil was wetted with ultrapure water to 60% MWHC, sealed by film and kept at 23 ℃ for 2 days. Then, the sample was wetted with ultrapure water to 100% MWHC and kept at the same temperature for 1 day. Before pressing the device onto the soil surface, soil paste was applied to the device window with a glass rod to avoid operational errors caused by inadequate contact. The device was deployed for 1 day at 23 ℃, then it

was gently removed from soil surface and immediately flushed with ultrapure water. Binding gel was removed and extracted with 8 mL of 1 mol HNO_3 for 1 day prior to measurement. The elution factor for Cd is 0.938 at 23 ℃ (Wang et al., 2016). The remaining soil was centrifuged at room temperature for 15 min at 4000 g. The supernatant was acidized with 5 M HNO_3 before being analyzed using ICP-MS.

The Cd concentrations determined using the DGT (C_{DGT}) were calculated as follows:

$$C_{DGT} = \frac{M\Delta g}{DAt} \tag{1}$$

Where M denotes the amount of Cd absorbed on the binding layer (mg), t is the deployment time (s), D is the diffusion coefficient of the metal ion at 23 ℃ (6.04 × E^{-6} cm^2 s^{-1} for Cd) (Wang et al., 2016), A represents the exposure area of the filter membrane (3.14 cm^2), and Δg is the total diffusional path length, i.e., the total thickness of the diffusive gel layer (0.80 mm) and the filter (0.45 μm) (Warnken et al., 2006).

2.4. DIFS simulation

As known, DIFS model is a useful tool for characterizing the release of trace metals in soils and sediments. In this study, the kinetic resupply of Cd in the samples was analyzed using DIFS simulations. The R-values obtained using Eq. (2) represent the ability of trace metals to dissociate from soil particles into pore water when the metal concentration on the DGT surface decreases. If the metal content on the surface of the DGT is solely supplied by diffusion in soil solution (i.e., there is no contribution from the labile solid phase), R reaches its minimum value (R_{diff}). R_{diff} values generated from the DIFS model and C_E were defined as the available content in the following equations:

$$R = \frac{C_{DGT}}{C_{soln}} \tag{2}$$

$$C_E = \frac{C_{DGT}}{R_{diff}} \tag{3}$$

Where R is an index of the extent to which pore water concentrations adjacent to the device are sustained at their initial value during the deployment, and therefore an index of the ability of the solid phase to resupply local pore water concentrations, $0 < R < 1$. In the sustained case, $R \to 1$ (Harper et al., 2000). C_E is the concentration that would have to be present in the soil solution to supply the same mass of metal accumulated by DGT if it was solely by diffusion (Zhang et al., 2001).

In the DIFS model, the distribution coefficient K_{dl} (Eq. (4)) (Lehto, 2016) and reaction time T_c (Eq. (5)) were used to calculate the adsorption and desorption rate constants, k_1 and k_{-1}, respectively:

$$K_{dl} = \frac{C_s}{C_{soln}} = \frac{1}{P_c} \frac{k_1}{k_{-1}} \tag{4}$$

$$T_c = \frac{1}{k_1 + k_{-1}} \tag{5}$$

$$P_c = \frac{W_1}{(W_0 - W_1)/\rho_w} \tag{6}$$

where C_s is taken as acid-exchangeable fraction (F1) extracted by the BCR method, and P_c is the soil particle concentration, soil samples are weighed as W_0 (g) and after drying at 105 ℃ are weighed as W_1 (g) and ρ_w is the density of water (g/cm^3). The required parameters for the DIFS model include P_c (g/cm^3), R, K_{dl} (cm^3/g), deployment time (h), soil porosity (ϕ_s), diffusion layer porosity (ϕ_d), the soil solution concentration C_{soln} (10^{-12} mol/cm^3) measured by the ICP-MS instrument, and the diffusion coefficients in the soil (D_s) and the diffusion coefficients in the diffusion layer (D_d) (Harper et al., 2000).

2.5. Quality control and statistical analysis

Different standard reference materials for soils (GBW07408, GSS-8), maize (GBW10012, GSB-3), and BCR (BCR 701) were analyzed in triplicate during digestion and extraction procedures. The average recoveries of Cd in the soil, plant, and BCR were 100.4%, 98.4%, and 97.9%, respectively. All containers were washed using 10% HNO_3 and flushed with ultrapure water before use. The detection limit of the ICP-MS for Cd was 0.2 ng/L. During extract procedures, solvent without sample was used as a blank control.

Kolmogorov–Smirnov method was used to test whether the data were normally distributed, otherwise logarithm transformation was applied make data conform to normality. Statistical analysis and linear fitting analysis were conducted using SPSS 20.0 and Origin 8.0 for Windows.

3. Results and discussion

3.1. Total concentrations of cadmium in samples

The properties of the soil samples were summarized in Table 1. The soil was mainly alkaline with pH values within the range 7.89–9.19, which is in accordance with previous studies in Tianjin (Meng et al., 2016). Both OM (0.73–2.78%) and CEC (12.11–41.33 cmol kg^{-1}) had a relatively wide range of values along with higher mean values, which may be due to the long-term application of fertilizers to agricultural soils. The total metal concentration of Cd in each research district was presented in Fig. 2. Cd concentrations in the maize samples were far below the national food standard (GB2762-2017, 2017), and the mean Cd content in maize samples followed the order of NHD<WQD<BDD<JHD. The concentration trends in both the soil and maize samples were consistent among these four regions, which implies
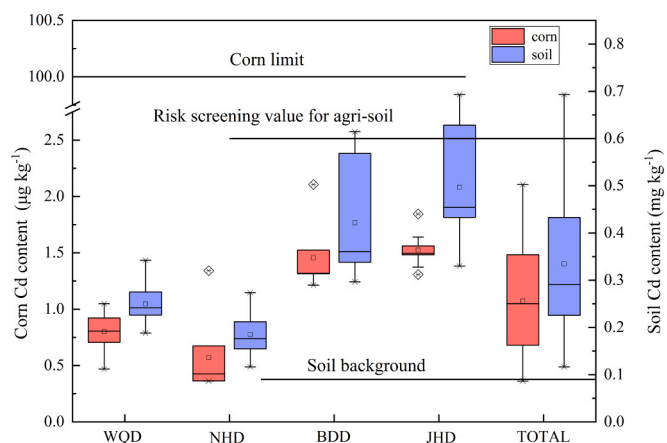

Fig. 2. Total content of Cd in soil and maize samples from different research districts.

that Cd contamination of the soil is one of the main factors contributing to metal accumulation in the maize. In contrast to the concentrations in the maize samples, the Cd content in all soil samples exceeded the background values for Tianjin. However, based on the soil risk control limit (GB15618-2018, 2018), 14.3% and 33.3% of sites in the BDD and JHD exceeded the risk control values, respectively.

The concentrations of Cd in soil and maize reported in other studies were shown in Table 2. The values obtained in Tianjin soils were similar to Volos, Greece (Antoniadis et al., 2019), although mean values were generally lower than reported elsewhere. The range of Cd concentrations in the maize samples was also relatively narrow compared to Guangxi and Liaoning (Gu et al., 2019; Lian et al., 2019), and the maximum and mean values were far lower than all other studies, although the minimum value was similar to Guangxi (Gu et al., 2019). These differences may due to the higher soil pH and OM content in Tianjin soils, with mean values of 8.53 and 15.01 g kg^{-1}, respectively, since soil pH and OM can reduce Cd uptake by plants. Where pH directly affects the Cd morphology in soil solution, higher pH makes less Cd available for migration and consequently less Cd available for plant uptake. The OM correlates with pH-dependent negative charge in soil, which causes cationic metals to be retained in the soil, resulting in lower Cd concentrations in the soil solution and reduced plant uptake. Moreover, only a small proportion of the Cd absorbed by maize reached the grain, and the ratio of Cd absorbed by the roots to Cd transported to the grain varied with different maize varieties. This reason may explain the variability in maize Cd concentrations between previous studies.

Table 1
Soil properties in the study area.

Sampling sites		pH	OM (%)	CEC (cmol·kg^{-1})
WQD	S1	8.89	0.73	12.11
	S2	8.85	1.17	15.26
	S3	8.89	0.97	16.57
	S4	9.06	1.26	30.55
	S5	8.66	1.62	41.33
	S6	9.14	1.06	15.90
	S7	9.19	1.65	17.22
	S8	8.79	1.37	20.68
	S9	8.54	1.06	16.46
	S10	8.34	1.47	13.66
	S11	9.16	1.19	15.71
	S12	8.76	1.65	17.95
NHD	S13	9.02	1.70	19.59
	S14	8.41	0.99	20.89
	S15	8.66	1.06	20.13
	S16	9.07	1.28	20.23
	S17	8.92	0.84	19.50
	S18	8.87	1.71	17.38
	S19	8.33	1.15	23.74
BDD	S20	8.45	2.10	23.36
	S21	8.19	1.79	15.30
	S22	8.53	1.87	20.66
	S23	8.21	2.78	31.43
	S24	7.93	1.48	12.54
	S25	7.88	1.84	23.93
	S26	7.94	1.73	23.18
JHD	S27	8.63	2.02	17.60
	S28	8.32	2.07	18.42
	S29	8.24	1.76	12.39
	S30	8.26	1.47	13.88
	S31	7.88	1.48	16.48
	S32	7.86	1.87	24.98
	S33	8.29	1.28	16.70
	S34	7.92	1.55	21.35
	S35	8.47	1.49	16.17

Table 2
C$_{total-Cd}$ in agricultural soil and maize samples.

Sampling site	C$_{total-Cd}$ (mg/kg)		References
	Soil	Maize	
Dongdagou, Gansu	14.9 ± 8.0	0.07 ± 0.07	(Li et al., 2015)
Xidagou, Gansu	5.6 ± 5.9	0.09 ± 0.08	(Li et al., 2015)
Volos, Greece	0.34 (0.14–0.69)	0.18 (0.06–0.12)	(Antoniadis et al., 2019)
Nanning , Guangxi	0.57 (0.09–5.84)	0.01 (0.0004–0.22)	(Gu et al., 2019)
Xi River watershed, Liaoning	1.36 (0.05–24.20)	0.28 (0.02–0.62)	(Lian et al., 2019)
Daye, Hubei	4.87 ± 6.43	0.21 ± 0.33	(Cai et al., 2019)
Punjab, India	0.94 ± 0.16	1.09 ± 0.02	(Sharma et al., 2018)
Huodehong, Yunnan	1.88 ± 1.24	0.80 ± 0.07	(Wang et al., 2015)
Tianjin	0.335 ± 0.152 (0.1166–0.6933)	0.0011 ± 0.0005 (0.0004–0.0021)	This study

3.2. Cd concentration in soils determined by chemical extractions and DGT

To investigate the Cd species associated with environmental risk, the extraction percentages of single and sequential methods were presented in Fig. 3. For the modified BCR extraction, the content ranges of acid-exchangeable Cd (F1), reducible Cd (F2), oxidizable Cd (F3), and residual Cd (F4) were 14.63–45.94%, 14.97–48.78%, 4.36–20.58%, and 10.2–53.73%, respectively. All the averaged proportions of F1, F2, and F4 were close to 30%, while the F3 accounted for about 10%. It was different from the results of other studies in which F4 accounted for more than 50% of the total metal content (i.e., Cu, Zn, and Ni) (Gao et al., 2018; Xu et al., 2018; Sun et al., 2019). These Cd extraction characteristics have also been reported in other studies (Xu et al., 2016; Soliman et al., 2018). The extraction of HNO_3 usually releases metals by destroying the soil matrix, including the total concentration adsorbed on soil OM, amorphous Fe/Mn oxides, and clay surfaces which is considered to be the adsorbable metal content in soils. $CaCl_2$ is a neutral salt and is the main component of the background soil electrolyte content. Potential toxic metals weakly adsorbed by electrostatic interactions and complexed with Cl^- are mainly released through Ca^{2+} exchange, which is less damaging to the soil structure and can extract exchangeable Cd. Thus, the extractability of HNO_3 was greater than that of $CaCl_2$.

R value is generally used to indicate the resupply capacity of the soil solid phase when the DGT-soil interface concentration decreases after DGT deployment, which can reflect the mobility of metals in soil to some extent. It is important for the absorption of metal by organisms that metal transfers from soil particles to the liquid phase. As a parameter representing the acid-exchangeable fraction as defined by sequential extraction, the MF (Section 2.2.2) has been widely accepted as an indicator of the relative mobility of metals in soil, which is directly associated with the uptake by plants. The bio-accumulation factor (BAF) has also been applied to represent the ratio of metals in maize to the corresponding soil content and, as such, is an intuitive description of metal mobility between soils and plants. As shown in Fig. 4, the BAF values were almost 100 times lower than R and MF values, indicating that the accumulation of metals in maize was related to soil properties, soil resupply, and complex uptake mechanisms of plants and root microorganisms. The migration of cadmium from the xylem to other parts of the plant was influenced by many factors. This may explain why the metal-accumulation efficiency of the grains of maize was much lower than the metal mobility in the soil. The average value of R was 15%, higher than that of the MF. This may be due to the fact that Cd dissociated from soil
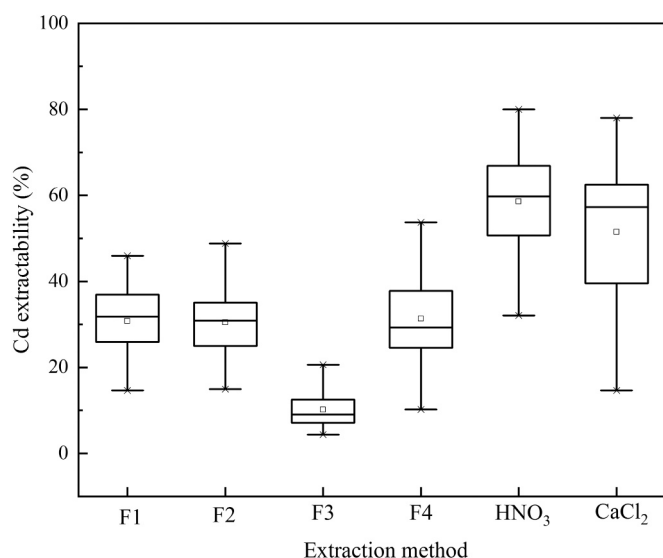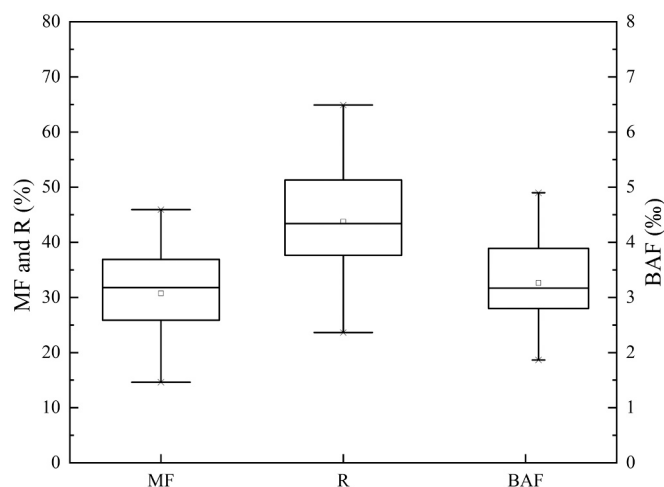

Fig. 4. Parameters for measuring the mobility of Cd.

particles into pore water during DGT deployment, whereas these dynamic processes were not considered in the chemical extraction based on equilibrium.

3.3. Correlation between maize Cd content and the measured Cd values using different methods

The linear relationship between maize Cd content and the obtained Cd values from different methods were shown respectively, in Fig. 5. The correlation coefficients of these measurements follow the order: DGT (0.92) >F1+F2 (0.88) ≈ soil solution (0.87)>HNO_3(0.85)> $CaCl_2$(0.81)>F1(0.80)>F2(0.73)> total content (0.72). It was notable that the fitting accuracy of the DGT method was greater than that of the soil solution and other chemical methods, and the F1+F2 of BCR method was slightly better than the soil solution method, which may be due to the higher exchangeable Cd content in the research districts. The weakest prediction capacity for total content indicated that soil bioavailability cannot ignore the interactions between the solid and liquid phases. The metal uptake of plants from the soil is generally completed by absorbing labile metals in the soil solution. Therefore, the metal content of a solution of saturated soil after centrifugation is related to the metal concentration in the plants. This was reflected in the fact that the soil solution method ranked third in predicting Cd content in the maize samples, which demonstrated that most of the factors related to metal uptake by plants were taken into consideration. However, soil solution method did not take into account the kinetics of labile metal dissociation from the solid phase.

When the concentration gradient caused by plant absorption is taken into consideration, the soil solution method cannot be considered as an appropriate method. Moreover, plants cannot absorb some metal species in the soil solutions and the original distribution of metals in soil solutions is disrupted by centrifugation. This is consistent with the result that the predictive ability of the DGT was greater than that of the soil solutions. F1+F2 had the lower coefficient of fit than the DGT method. However, F1+F2 method had better precision for Cd in the maize samples compared to other chemical extractions, and the bioavailability of Cd in the studied soils could be characterized by the acid-exchangeable and reducible fractions as defined by the BCR method. The prediction ranking of the general extractions was lower than those of the DGT method and was consistent with their extractabilities in soil. This provides evidence that the single extractions had the disadvantage of not accounting for the effects of soil characteristics.

The Cd concentrations in the maize samples showed the highest correlation coefficient with C_{DGT}, and the previous studies of Sb, As and Cu in plants have reached similar conclusions (Zhang et al., 2001, 2018;

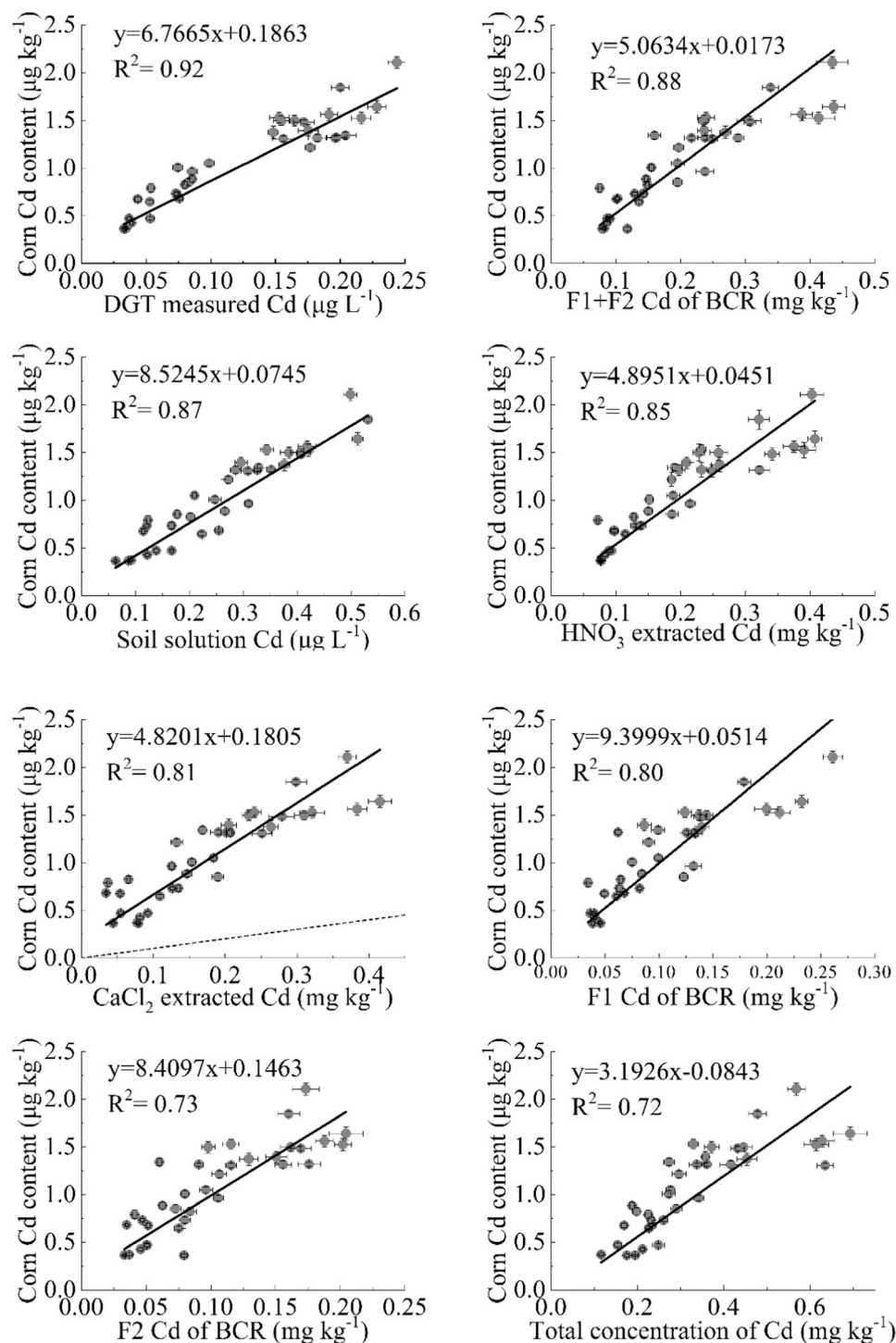**Fig. 3.** Extraction percentages of single and sequential methods.

Fig. 5. The relationship between the maize Cd content and the measured Cd values from different methods.

Dai et al., 2018). The concentration gradient established between the DGT and soil interface led to depletion of the soil solutions and resupply of the solid phase. This process was similar to the uptake of heavy metals from soils by plant roots. These results indicated that the measurement of DGT involved the exchange kinetics at the interface of soil solid-liquid phase, and DGT can simulate the uptake of heavy metals by plant roots. Although DGT currently has some shortcomings, it can still be applied as a reliable method for predicting the bioavailability of Cd to maize and has the potential for the application in ecological risk assessments. The results of this study showed that the soil solid phases played an important role in defining the available metal content of the soils. To further

evaluate the risk of soil contamination, investigation of the Cd release patterns from soil samples was conducted.

3.4. Cd dissociation kinetics simulated by DIFS model and analysis of release mechanism

DIFS model was used to simulate the characteristics of metal remobilization and obtain the dissociation parameters correlated with resupply from the solid phase (Table 3). T_c indicates the rate constants as a response time of the exchange reaction, which represent the characteristic time for the perturbed system to reach 63% of its equilibrium

Table 3
Parameters of Cd determined by DIFS model.

Sampling sites		MWHC (%)	K_{dl} (cm^3/g)	T_c (s)	k_{-1} (s^{-1})	k_1 (s^{-1})	R	R_{diff}	C_E (mg/L)
WQD	S1	52.43	266.20	912.70	1.63E-06	1.09E-03	0.30	0.04	1.82
	S2	46.76	693.49	308.90	2.19E-06	3.24E-03	0.47	0.05	1.79
	S3	50.66	677.28	122.90	6.47E-06	8.13E-03	0.61	0.05	1.43
	S4	51.61	277.23	204.40	6.20E-06	4.89E-03	0.43	0.03	1.86
	S5	34.96	216.77	1057.00	2.62E-06	9.43E-04	0.32	0.04	1.31
	S6	48.14	316.89	777.00	1.68E-06	1.29E-03	0.32	0.04	1.97
	S7	52.27	319.41	340.70	3.12E-06	2.93E-03	0.39	0.04	2.14
	S8	41.88	377.24	509.90	3.53E-06	1.96E-03	0.44	0.06	1.26
	S9	44.75	474.11	296.70	3.44E-06	3.37E-03	0.47	0.05	2.07
	S10	46.20	426.23	1874.00	7.73E-07	5.33E-04	0.28	0.06	1.54
	S11	33.54	271.08	2217.00	8.62E-07	4.50E-04	0.24	0.04	1.40
	S12	43.32	303.68	691.50	1.60E-06	1.44E-03	0.30	0.03	2.65
NHD	S13	45.16	288.64	1119.00	1.19E-06	8.92E-04	0.27	0.03	1.20
	S14	34.72	607.37	205.00	4.41E-06	4.87E-03	0.52	0.04	0.86
	S15	45.75	214.71	2386.00	8.11E-07	4.18E-04	0.32	0.03	1.19
	S16	42.79	432.35	576.10	2.01E-06	1.73E-03	0.38	0.04	1.19
	S17	41.47	490.81	679.00	1.68E-06	1.47E-03	0.38	0.04	0.88
	S18	43.76	525.71	518.10	1.64E-06	1.93E-03	0.38	0.03	0.98
	S19	35.81	302.00	53.88	3.14E-05	1.85E-02	0.62	0.05	4.14
BDD	S20	49.93	465.62	76.26	1.66E-05	1.31E-02	0.64	0.05	3.48
	S21	37.47	523.67	181.70	3.45E-06	5.50E-03	0.49	0.04	6.67
	S22	56.97	332.75	29.02	3.48E-05	3.44E-02	0.65	0.05	3.24
	S23	40.04	176.05	42.50	6.97E-05	2.35E-02	0.56	0.05	4.00
	S24	38.39	386.18	66.31	1.30E-05	1.51E-02	0.60	0.05	3.82
	S25	42.24	291.76	56.06	2.05E-05	1.78E-02	0.59	0.05	3.52
	S26	51.31	503.09	277.30	4.53E-06	3.60E-03	0.51	0.06	3.90
JHD	S27	52.16	413.14	559.80	2.44E-06	1.78E-03	0.45	0.05	4.41
	S28	45.84	528.36	131.60	8.08E-06	7.59E-03	0.38	0.04	4.87
	S29	47.98	371.55	335.60	2.62E-06	2.98E-03	0.39	0.04	3.95
	S30	53.12	356.95	336.10	3.35E-06	2.97E-03	0.43	0.04	3.69
	S31	52.46	432.91	209.00	4.95E-06	4.78E-03	0.51	0.05	3.34
	S32	55.80	338.39	504.60	3.48E-06	1.98E-03	0.42	0.05	3.52
	S33	44.72	361.01	295.40	3.78E-06	3.38E-03	0.44	0.04	3.47
	S34	52.18	355.11	579.10	2.34E-06	1.72E-03	0.38	0.05	3.12
	S35	41.39	477.04	374.00	3.06E-06	2.67E-03	0.46	0.05	3.58

position. K_{dl} is a distribution coefficient based on the labile solid-phase components that can be exchanged with the solution phase (Harper et al., 2000). T_c and K_{dl} were used to describe the adsorption kinetics (k_1) and desorption kinetics (k_{-1}) and the range of k_{-1} was 1.19E-06–8.62E-06. k_{-1} of S10 and S11 for WQD, S19 for NHD, and S21 and S26 for BDD were an order of magnitude smaller or larger than other sites in the same region, and such differences were also reflected in T_c, but the variation in K_{dl} was irregular. The results of the correlation analysis also showed that the correlation coefficient between K_{dl} and k_{-1} was −0.33 with a p value of 0.025, which was a significant negative correlation, while the correlation coefficient between T_c and k_{-1} was −0.412 with a p value of 0.007, which was a highly significant negative correlation, indicating that the correlation between k_{-1} and T_c was better. k_{-1} value is 100 or 1000 times lower than k_1 value (Table 3). The kinetic rate depends not only on the rate constant, but also on the reactant concentration, thickness of the diffusion gel, and temperature. Since the thickness of the diffusion gel and temperature were within the permissible range and remained constant, and the reactant concentration did not alter much, the effects of these factors were neglected in this study. Therefore, the rate of desorption was significantly lower than the rate of Cd depletion in the soil pore water. These results indicated that the dissociation of labile Cd from soil particles was a relatively slow process, which may be due to the formation of metal oxides and organic complexes caused by the high pH and OM content of these soils.

R represents the release capacity of soil solid-phase metals. The average R value of BDD (0.58) was significantly higher than soils in other areas, indicating a high potential for Cd release from soils in the area, but the maximum R value for all sites was only 0.65, implying that the sampled soils may not be sufficient to maintain a sustained supply of Cd for resupply. R was influenced by parameters such as K_{dl}, T_c and k_{-1}, the K_{dl} of all collecting sites ranged from 176.04 cm^3/g to 693.49 cm^3/g and was more than 300 cm^3/g at 28 sites, indicating that soil samples

from most areas had a high potential for release of Cd from the solid phase to pore water. The K_{dl} was similar in S2 and S3, while the other parameters were quite different, with a 1.52-fold difference in T_c and a 1.95-fold difference in k_{-1}. Such phenomena were also observed in S6 and S7, S5 and S12, S13 and S19, and S10 and S20. This suggested that K_{dl} affected R to a different extent to T_c and k_{-1}, and the effects of T_c and k_{-1} on the dynamic release of soil solid phase may also be different. The results of the correlation analysis showed that the correlation coefficients of K_{dl}, T_c, k_{-1} and R were 0.3, −0.82 and 0.59, respectively, and the p value was less than 0.05, showing a significant correlation. It indicated that there was an association between these three parameters and R. However, in the stepwise regression process, K_{dl} was excluded as a variable. The absolute values of the modified coefficients of T_c and k_{-1} were 0.7 and 0.3, respectively, indicating that the R value was more sensitive to T_c than k_{-1}. This result has also been reported in previous studies.

The relationship between the R values simulated by the DIFS model and the deployment time was shown in Fig. 6. Overall, the R values increased rapidly during the first 30 min, to the maximum after approximately two hours, and then tended to flatten or gradually decline. This is mainly due to the adsorption of heavy metals by the binding gel at the beginning of DGT deployment causing the rapid diffusion of metals and desorption of solid phase metals in the soil solution. The diffusion layer was initially devoid of Cd metals, and when DGT came into contact with the soil solution, a porosity-related metal concentration gradient was rapidly established, leading to a rapid rise in R. The faster the metal dissociation rate, the faster the diffusion in the soil solution, the shorter the rise time of R. This period is mainly influenced by the water content of the soil. The 31 curves in Fig. 6 showed a smooth trend after reaching the peak, indicating that after a stable concentration gradient was established in the diffusion layer, the resupply of soil at the corresponding sites can satisfy the partial metal
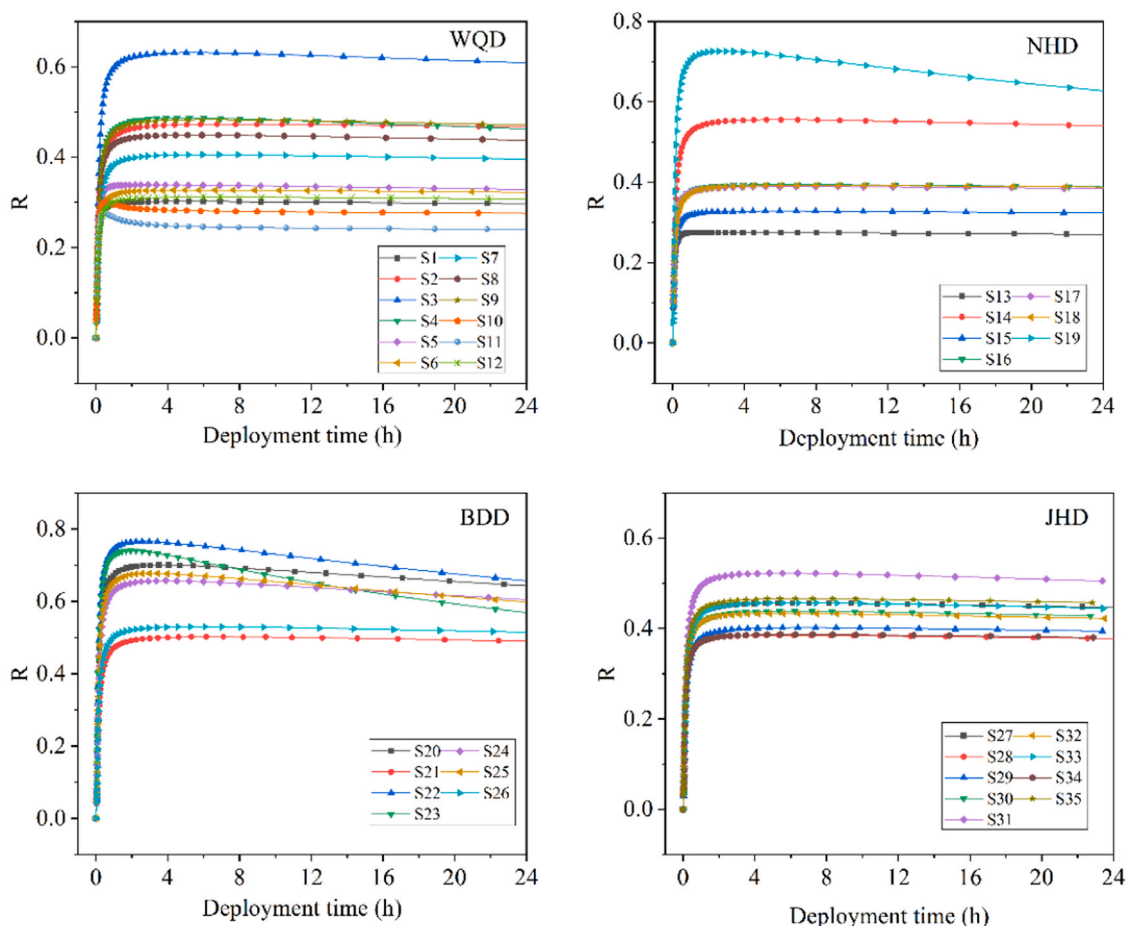
Fig. 6. Trend of R values with deployment time.

demand of DGT. This situation cannot completely satisfy the concentration of DGT depletion, but it also reached a relative balance between the depletion rate and the resupply rate, so this mode was called the apparent steady state.

The S11, S19, S22 and S23 curves showed a decreasing trend after reaching their peaks, indicating that the contribution of soil solids to the DGT device to maintain metal consumption was unable to sustain the flux and the supply rate was progressively slower than the consumption rate of Cd, approaching zero. Therefore, these sites were described as non-steady-state of the partially sustained case. However, even for non-steady-state sites, their R decreased by less than 30% over the course of the 24 h, suggesting that their labile metal pools can still maintain a relatively stable release, and that soil particles can still release metal into solution with the establishment of a concentration gradient. The larger the decrease in R, the smaller the amount of labile Cd bound to the soil solid phase. For the apparent steady state curve, there were five sites with peaks greater than 0.6 in BDD while the other districts had 2 sites with a peak above 0.6, indicating the resupply capacity of Cd to soil in BDD was relatively higher than in other regions, but the overall resupply capacity was lower.

Overall, the release of Cd in the studied area was stable, but the R values were relatively low. This also likely explained the low levels of metal enrichment in the maize samples. However, stable and persistent labile metal pools in these soils may still pose potential environmental risk through the accumulation of bioavailable metals during long-term crop cultivation, irrigation and rainfall.

4. Conclusions

The research results demonstrated that the total concentration of Cd in the soil samples exceeded the background value, and Cd in the maize samples were far below the national food standard. Compared with other analysis and extraction methods, bioavailable Cd measured by DGT correlated well with Cd in maize grains ($R^2 = 0.92$), indicating that DGT can predict the uptake of Cd by maize more accurately. The total Cd content in soils was generally low (0.34 mg kg^{-1}) in the studied area, but the release of Cd was stable, suggesting that labile Cd in soil still poses a risk to crops during long-term cultivation in these areas. In future studies, DGT and DIFS models can also be considered to quantitatively predict the release amount of heavy metals in regional farmland soil.

CRediT authorship contribution statement

Rui Chen: Conceptualization, Supervision, Writing - review & editing. **Tao Gao:** Conceptualization, Supervision, Writing - original draft, review & editing. **Nuo Cheng:** Conceptualization, Supervision, Writing - review & editing. **Guoyu Ding:** Conceptualization, Supervision, Writing - review & editing. **Qi Wang:** Conceptualization, Supervision, Writing - review & editing. **Rongguang Shi:** Resources, Supervision. **Guangzhi Hu:** Resources, Supervision. **Xuying Cai:** Software, Formal analysis, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2020.124837.

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