

## Article

# Change of the Extractability of Cadmium Added to Different Soils: Aging Effect and Modeling

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**Abstract:** Ethylenediaminetetraacetic acid (EDTA) is known to be a chelating agent and has been widely used for estimating the total extractable metals in soil. The effect of aging on EDTA-extractable cadmium (Cd) was investigated in five different soils at three Cd concentrations incubated for 180 days. The EDTA-extractable Cd rapidly decreased after incubated during 30–60 days, followed by slow processes, and for 90 days the EDTA-extractable Cd tended to be stable. The decrease in EDTA-extractable Cd may be due to precipitation/nucleation processes, diffusion of Cd into the micropores/mesopores, and occlusion within organic matter in soils. A semi-mechanistic model to predict the extractability of Cd during incubation, based on processes of Cd precipitation/nucleation, diffusion, and occlusion within organic matter, was developed and calibrated. The results showed that the processes of micropore/mesopore diffusion were predominant processes affecting the extractability of Cd added to soils, and were slow. However, the proportions of the processes of precipitation/nucleation and occlusion within organic matter to the non-EDTA-extractable Cd added to soils were only 0.03–21.0% and 0.41–6.95%, respectively. The measured EDTA-extractable Cd from incubated soils were in good agreement with those predicted by the semi-mechanistic model ( $R^2 = 0.829$ ). The results also indicated that soil pH, organic matter, and incubation time were the most important factors affecting Cd aging.

**Keywords:** aging; cadmium; ethylenediaminetetraacetic acid; semi-mechanistic model; soil

## 1. Introduction

Various extractants such as water, organic acids, neutral electrolytes, and synthetic chelating agents have been usually utilized to measure the availability of soil metals to plants. Several authors have hypothesized that the application of models with metals extraction data might better reflect behaviors of metals in soils [1–5]. For a given chemical extractant, the extraction method generates two kinds of data: (i) with respect to the total metals content, the proportion of extractable metals in the soil sample; and (ii) the dynamics of metals [6]. In view of the effectiveness in removing a wide range of heavy metals, chelating or acidic agents are widely applied as extractants [7]. As a well-known strong chelating agent, ethylenediaminetetraacetic acid (EDTA) has been widely applied to estimate the total extractability of metals [8,9], and reported to extract metals that are associated with oxides and secondary clay minerals and organically bound [10]. Metals extracted by EDTA are considered to be good indicators for the maximum potential metal extractability, helpful for the prediction of long-term risks [6] and useful for modeling the dynamics of metal ions and predicting their availability to plants and animals.

A number of studies have noted a decrease in the extractability or potential availability of cadmium (Cd) added to soils over time [11–14]. When water-soluble Cd is spiked to soils, several reactions may take place immediately: it partitions quickly between soil solution and solid phases, followed by further, slow processes that decrease the extractability and availability/toxicity of added Cd. The rapid adsorption of soluble metal to soil solid surfaces via forming outer sphere (electrostatic or physical) complexes driven by the difference in the concentration gradient from the solution phase to the surface of soil minerals and negatively charged organic matter, initiated the fast retention [14–16]. It was reported that after soluble Cd was added to a soil with high clay content and (60%) high organic matter, 80% of adsorption occurs within 10 min [17]. For the adsorbed Cd, the longer the contact with the soil, the stronger the chemical bond formed or more stable solid phase formed, and this may be a result of a rearrangement of Cd on the surface of the solid phases, e.g., diffusion of Cd into micropores on the surface of soil minerals or organic materials [16]. An additional hypothesis is that the Cd that has been adsorbed gradually diffuses from the surface of soil minerals into the crystalline structure [18]. After the rapid absorption, a secondary (slow) migration of Cd from outer- to inner-sphere, including the surface of soil minerals (residual forms), iron (Fe)/manganese (Mn) oxides and carbonates may take place [14,19]. Further incubation may result in more extensive shifts over time, including mesopore/micropore diffusion, cavity entrapment, occlusion within solid phases by organic or inorganic materials, and surface precipitation/crystal growth [20–24]. The extractability of a metal in soil is dramatically influenced by the specific mechanisms of a metal's interaction and retention by soil, and the resultant geochemical stability of the solid phase constituents [25]. The time needed to attain an apparent equilibrium may be significantly affected by organic content, soil pH, Fe/Mn oxides, and clay minerals. In all soil, the solubility of Cd is greatly affected by soil pH; in alkaline soil, precipitation is likely to account for Cd equilibria; and in acid soil, the Cd activity may largely be governed by soil organic matter and sesquioxides [26].

Many chemical models based on the total/extract have been developed to predict the changes in metal added to soils. Streak and Richter [27] used EDTA (0.025 M)-extractable Cd and zinc (Zn) to model the transport of Cd and Zn in a sandy soil. Labanowski et al. [6] modeled the mobilization of EDTA- and citrate-extractable metals, such as Cd, lead (Pb), Zn, and copper (Cu), and EDTA-extractions were hypothesized to be more predictive for long-term metal migration with depth. Proffit et al. [28] used synthetic models to simulate aging of Cu contamination in soils over time. Semi-mechanistic models (the combination of mechanistic models and empirical models) have also been developed using soil properties to predict the potential availability pool of metals in soils. Ma et al. [23,29] developed two semi-mechanistic models to predict the short- and long-term aging of Cu added to soils respectively based on incubation time, pH, and organic carbon (OC). The models were validated as reasonable, and successfully predicted the exchangeability of Cu added to soils. Subsequently, the semi-mechanistic models of Ma et al. [23,29] were successfully used in cobalt (Co) and nickel (Ni) aging processes predicted after added to a wide range of soils, with reasonably accurate results [25,30]. Because of the incorporation of mechanistic or semi-mechanistic sorption concepts, the semi-mechanistic models are more robust than strict empirical models (regression models) of contaminant behavior, and moreover, owing to their scientific defensibility, they are of particular interest to regulatory agencies [25,31].

Since long- and short-term reactions modify Cd extractability and toxicity with time, they are significant in considering the risk from various anthropogenic sources additions of Cd to soils [32]. However, for the risk assessment of metals in soil, current environment criteria, and protocols do not take into account the influence of aging on extractability and toxicity of metals [32,33]. In the present study, the extractability of added Cd in five different soils incubated for 180 d was determined using EDTA as an extractant, and used to develop a new semi-mechanistic model based on incubation time, soil pH, and OC to predict the extractability of Cd to describe the change processes. The model was validated by testing it against the five soils with varying physiochemical properties and dosed with soluble Cd at three levels, and the extractability of Cd added to soils was successfully predicted.

## 2. Materials and Methods

### 2.1. Soil Samples and Treatments

The data in this paper were collected from previous studies of dynamic characteristics and aging factors of Cd added to soils [34]. Five unpolluted soils with different physiochemical properties were collected from northern to southern China. Soil physical and chemical properties including the background Cd content in soils are shown in Table 1. Soil pH and electrical conductivity (EC) were determined in a water suspension of soil using a 5:1 ratio (deionized water:soil) [35]. Soil organic carbon (OC) content was determined as the difference between total and inorganic carbon contents [36,37]. Cation exchange capacity (CEC) was determined using the ammonium chloride method [35]. Free Fe oxides (Fe<sub>OX</sub>) were determined using a dithionated-citrate extraction [38]. Soil clay content was analyzed using the sedimentary method [39]. The background Cd in the five soils was measured with inductively coupled plasma atomic mass spectrometry (ICP-MS) after digesting unpolluted soil samples (<0.25 mm) with an aqua regia (1:3 fresh mixture of concentrated HNO<sub>3</sub> and HCl) digestion.

**Table 1.** Selected physical and chemical properties of soils.

| Soil Code | Soil Location | Soil Type     | pH (H <sub>2</sub> O) | OC (%) | CEC (cmol kg <sup>-1</sup> ) | EC (μS cm <sup>-1</sup> ) | Fe <sub>OX</sub> (g kg <sup>-1</sup> ) | Cd (mg kg <sup>-1</sup> ) | Clay (<0.002 mm, %) |
|-----------|---------------|---------------|-----------------------|--------|------------------------------|---------------------------|--|---------------------------|---------------------|
| HN        | Hunan         | Red soil      | 4.54                  | 0.87   | 7.47                         | 74.2                      | 3.76                                   | 0.121                     | 46.1                |
| ZJ        | Zhejiang      | Paddy soil    | 6.72                  | 2.46   | 12.82                        | 203.4                     | 2.14                                   | 0.119                     | 38.9                |
| CQ        | Chongqing     | Purple soil   | 7.02                  | 0.99   | 22.31                        | 71.3                      | 3.1                                    | 0.207                     | 27.3                |
| JL        | Jilin         | Black soil    | 7.31                  | 2.17   | 28.81                        | 147.1                     | 1.26                                   | 0.142                     | 44.6                |
| HB        | Hebei         | Alluvial soil | 7.81                  | 0.63   | 6.36                         | 5.7                       | 0.98                                   | 0.172                     | 19.1                |

Soil samples were air-dried, ground, and passed through a 2-mm mesh sieve. Soil samples equivalent to 1 kg were transferred into polyvinyl chloride canisters. Cd was added at different times (1, 90, 120, 150, 166, and 180 d) using a suitable aqueous solution of 3CdSO<sub>4</sub>·8H<sub>2</sub>O to artificially increase the total soil Cd concentration by 0.6, 1.2, or 2.4 mg kg<sup>-1</sup>. After Cd addition, the soils were thoroughly mixed, and the soil moisture adjusted to 70% of their water-holding capacities by adding double distilled water weekly (weight of canister and sample). All treatments were conducted in triplicate, and incubated at 25 °C in a greenhouse. After incubation, soil samples were collected from canisters (as a column from soil surface to bottom).

### 2.2. Determination of EDTA-Extractable Cd

Subsamples of 1.00 g were weighed into 50 mL digestion tubes and mixed end over end for 2 h with 25 mL of 0.05 M Na<sub>2</sub>-EDTA. Then the suspensions were centrifuged at 4000 × g for 20 min and filtered through 0.45 μm pore-size cellulose acetate filters before analysis [40]. The Cd concentrations in the extraction solutions were measured using ICP-MS (Agilent 7500a, Agilent Technologies Co. Ltd., Santa Clara, CA, USA). For quality control of chemical analysis, standard certified reference soil materials were applied for determination of total Cd concentrations and of physical–chemical properties of soils.

The ratio of the content of EDTA-extractable Cd to the added Cd content denotes *EDTA-Cd* (%), and was used for the semi-mechanistic model to predict the changes in EDTA-extractable Cd. This chosen parameter should allow a direct evaluation of Cd in equilibrium with soil solution (and therefore potentially available) and is consequently well suited to be expressed with a semi-mechanistic model based on processes that remove Cd from the mobility pool. The concentration of EDTA-extractable added Cd and *EDTA-Cd* (%) were calculated using the equations

$$C_t = C_{ta} - C_{t0} \quad (1)$$

$$EDTA - Cd(\%) = \frac{C_t}{C_{add}} \quad (2)$$

where  $C_t$  ( $\text{mg kg}^{-1}$ ) is the concentration of EDTA-extractable added Cd after incubation for  $t$  days;  $C_{ta}$  ( $\text{mg kg}^{-1}$ ) is the concentration of EDTA-extractable total Cd after incubation for  $t$  days;  $C_{t0}$  ( $\text{mg kg}^{-1}$ ) is the concentration of EDTA-extractable Cd with no exogenous Cd added after incubation for  $t$  days; and  $C_{add}$  ( $\text{mg kg}^{-1}$ ) is the concentration of Cd added to soils.

### 2.3. Considerations for the Model to Predict EDTA-Extractable Cd

After water-soluble Cd is spiked to soils, the added Cd decreases in extractability and availability/toxicity and shifts to less mobile forms through processes of precipitation/nucleation, mesopore/micropore diffusion, and occlusion within organic matter. The fraction of EDTA-Cd (%) during aging processes can be expressed by the equation

$$EDTA - Cd(\%) = (1 - Y_1 - Y_2 - Y_3) \times 100\% \quad (3)$$

where  $Y_1$ ,  $Y_2$ , and  $Y_3$  represent the change (fraction) in EDTA-extractable Cd of added Cd attributed to the processes of precipitation/nucleation, mesopore/micropore diffusion, and Cd occlusion within organic matter, respectively.

#### 2.3.1. Processes of Precipitation/Nucleation

Rapid adsorption reactions would not decrease the EDTA-Cd (%) as the adsorbed Cd would still be EDTA-extractable. However, the aging processes, which are especially rapid at high pH and can result in decreases in the extractability of added Cd (EDTA-Cd, %), are most likely due to the surface precipitation/nucleation of Cd-bearing soil minerals [12]. These precipitation/nucleation processes are considered to be connected with the formation of  $\text{Cd}(\text{OH})^+$  on soil Fe oxides and clay minerals [19,41]. Although the Cd precipitates/surface precipitates have been assumed, they are not or have rarely been found in normal soils. The processes of precipitation/nucleation can be expressed as [23,29]

$$Y_1 = \frac{B}{10^{(pk^0 - pH)} + 1} \times t^{\frac{C}{t}} \quad (4)$$

where  $Y_1$  represents the changes (fraction) in EDTA-Cd (%) of added Cd because of the rapid processes of precipitation/nucleation;  $B$  is a coefficient considered to express the effect of precipitation/nucleation;  $t$  is aging time (d);  $pk^0$  is the first hydrolysis constant of Cd; the equation  $t^{\frac{C}{t}}$  ( $C$  is a constant) describes the kinetics of the rapid processes; and  $pH$  is soil pH. Since the precipitation/nucleation processes only take a very short period of time, they have little temperature reliance [42]. This equation has worked very well when used to predict the aging processes of other metals, e.g., Cu, Co, and Ni [25,29,30]. Thus, we used this equation to predict the precipitation/nucleation processes after soluble Cd added to soils.

#### 2.3.2. Processes of Mesopore/Micropore Diffusion

Previous studies showed that in short-term aging, the precipitation/nucleation are predominant processes in soils with relatively high pH; while in soils with low pH, aging is mainly attributed to diffusion processes [16]. In long-term aging, the diffusion processes dominate aging at all pH conditions, but precipitation/nucleation processes also play dominant roles at high soil pH. To predict the aging process precisely, Ma et al. [23,29] developed two semi-mechanistic models with a simplified description of the respective diffusion processes for short- and long-term aging. The diffusion processes are linearly relevant to the square root of time ( $t^{1/2}$ ) in the short-term model; and diffusion processes are linearly relevant to the natural logarithm of time,  $\ln(t)$ , in the long-term model. Both short- and long-term models show good results, and have been widely applied in other studies of aging processes [25,28,30,43].

The diffusion of Cd ions into mesopores/micropores on soil surfaces can be regarded as Cd ions diffusing into the plane sheet of the mesopores/micropores. Microporous materials, such as layered

aluminosilicates, are major participants in diffusion processes. Compared with the soil volume, the solution volume is relatively smaller, and so the concentration of the solute would decrease during diffusion. Therefore, the processes can be expressed as “diffusion in a plane sheet from a stirred solution with limited volume”. If the thickness of the plane sheet where micropores occur is assumed to be at  $2l$ , the position of micropores in the space is  $-l \leq x \leq l$ , the position of the limited volume of the Cd solution is  $-l - a \leq x \leq l + a$ , the initial concentration of Cd in this plane is 0, the concentration of Cd in solution is  $C_0$  and, based on Fick's first and second law of diffusion, can be expressed by the equation

$$\frac{\partial C}{\partial t} = D \times \frac{\partial^2 C}{\partial x^2} \quad (5)$$

According to Crank's research on diffusion, Equation (5) can be expressed as

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp(-Dq_n^2 t/l^2) \quad (6)$$

where  $q_n$  represents the non-zero positive root of the equation:  $\tan q_n = -\alpha q_n$ ,  $\alpha$  ( $\alpha = a/l$ ) is a constant whose value can be evaluated by the fraction of total amount of Cd finally taken up by soils ( $K = \frac{1}{1+\alpha}$ ,  $K$  is the fraction of amount of Cd taken up by soil to the amount of Cd added to soil),  $M_t$  is the total amount of Cd in this plane when the diffusion time is  $t$ , and  $M_\infty$  is the total amount of Cd in this plane when the diffusion time is infinity.

In most cases, Equation (6) can be simplified as

$$\frac{M_t}{M_\infty} = (1+\alpha) \left\{ 1 - \exp(T/\alpha^2) \times \operatorname{erfc} \sqrt{T/\alpha^2} \right\} \quad (7)$$

where  $T = Dt/l^2$ ,  $t$  is incubation time (d), and  $\operatorname{erfc}$  refers to complementary error function.

Finally, the total exogenous Cd will completely enter into soils in the aging process, and  $M_\infty$  is the total amount of added Cd. Thus,  $Y_2$  can be described by the form

$$Y_2 = (1+\alpha) \left\{ 1 - \exp(T/\alpha^2) \times \operatorname{erfc} \sqrt{T/\alpha^2} \right\} \quad (8)$$

where  $Y_2$  represents the change (fraction) in EDTA-Cd (%) of added Cd attributed to the diffusion processes.

After the aging process, almost all exogenous Cd will be retained in soil, and  $\alpha$  tends to 0, then Equation (8) can be expressed as

$$Y_2 = 1 - \exp(T/\alpha^2) \times \operatorname{erfc} \sqrt{T/\alpha^2} \quad (9)$$

where  $D$ ,  $l$  and  $\alpha$  are constants, and we can suppose that  $F = D/(\alpha^2 l^2)$ , then Equation (9) can be expressed as

$$Y_2 = 1 - \exp(Ft) \times \operatorname{erfc} \sqrt{Ft} \quad (10)$$

### 2.3.3. Processes of Occlusion within Organic Matter

The processes of Cd occlusion within organic matter is affected by the amount of binding sites on organic matter in soil, so there is a linear relationship between the amount of organic matter and the processes of Cd occlusion within organic matter [14,16]. These processes of Cd occlusion within organic matter can be expressed as

$$Y_3 = G \times \left( \frac{C_{org}}{100} \right) \times t^{H/t} \quad (11)$$

where  $Y_3$  represents the change (fraction) in EDTA-Cd (%) of added Cd due to the Cd occlusion within organic matter;  $G$  is a constant that is relevant to the effect of occlusion processes; and  $C_{org}$  is total

OC content of soils (% *w/w*). The equation  $t^{H/t}$  expresses the relatively fast occlusion processes. In this case, we also ignored the effect of temperature on the fast processes of Cd occlusion within organic matter.

### 3. Results and Discussion

#### 3.1. Change of EDTA-Extractable Cd in Different Soils with Time

The changes in EDTA-extractable Cd (*EDTA-Cd*, %) extracted by 0.05 M EDTA in five different soils collected from Hunan (HN), Zhejiang (ZJ), Chongqing (CQ), Jilin (JL), and Hebei (HB) at three Cd added concentrations (0.6, 1.2, and 2.4 mg kg<sup>−1</sup>) with different incubation times are summarized in Figure 1. The data in Figure 1 were calculated from the raw data reported in previous studies of dynamic characteristics and aging factors of Cd added to soils [34]. The *EDTA-Cd* increased initially due to the addition of water-soluble Cd in all five soils, and decreased with increasing incubation time. Compared to 14 d, for all five soils the *EDTA-Cd* decreased by 21.5–38.0% at 30 d, and 47.8–54.8% at 60 d. After the initial rapid retention, there was a continuing but slow reaction of soluble Cd with soil that gradually reduced the EDTA-extractable Cd over time. During 90–180 d, the *EDTA-Cd* decreased within a range of 6.3–18.1% in all soils. To reach equilibrium among soil solid and solution phases, the rate of slow retention also decreased over time. In summary, the EDTA-extractable Cd rapidly decreased after incubation for 30–60 d, driven by the difference in the concentration gradient from the soil solid phases to solution; this was followed by slow processes, and for 90 d the EDTA-extractable Cd tended to be stable. Further aging may lead to more large changes, including diffusion and occlusion within organic or inorganic materials [20], the development of a surface precipitation and nucleation [44]. However, some researches show that slow sorption or fixation of Cd in soil is not very notable [45,46]. Cadmium sorption in two Danish soils (loamy sand, sandy loam) was reversible since the Cd adsorption and desorption isotherms overlap, even when the soils were air dried or incubated at 1 °C for 67 weeks after loading the soils with Cd [45]. Smolders et al. [46] measured the isotopically exchangeable Cd (*E* value) in 10 Belgian agricultural soils, and showed that the %*E* value ranged from 62% to 90% in 8 soils, and Cd fixation is not very pronounced. No explanation can yet be given for the difference between the two results.

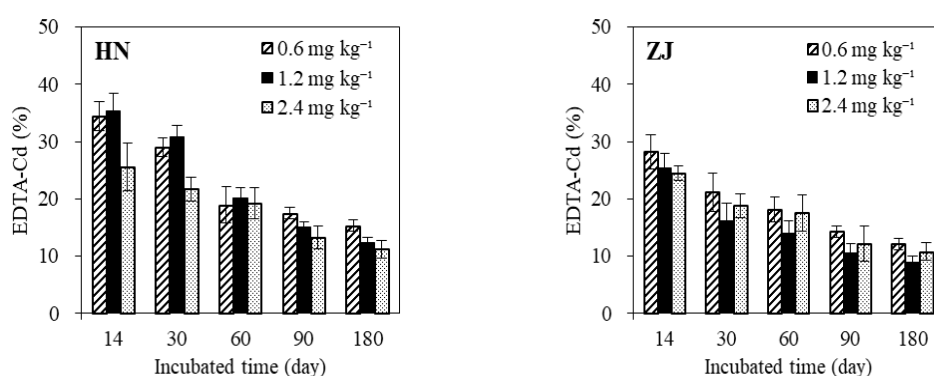
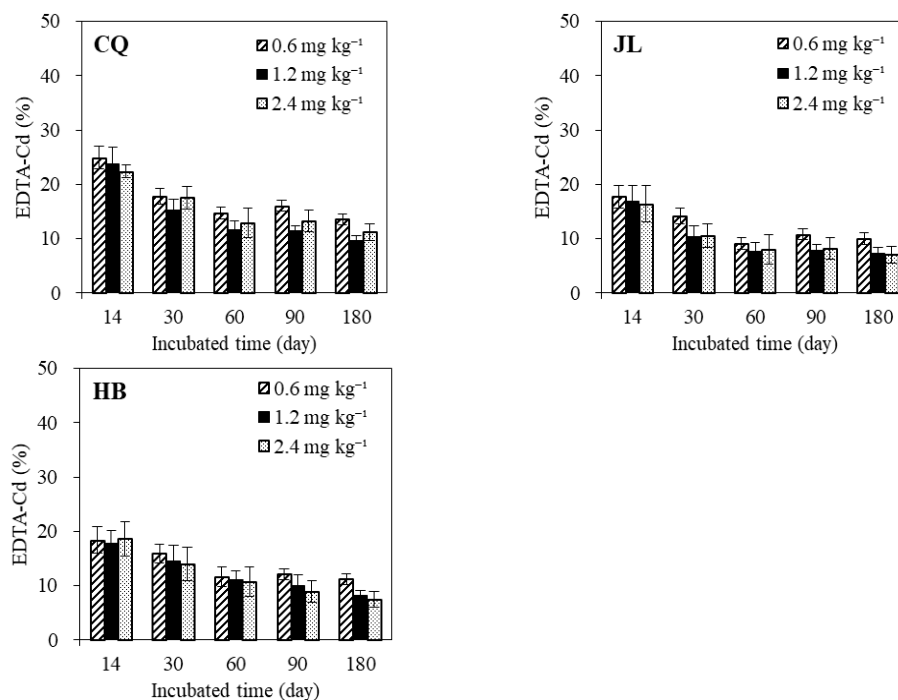


Figure 1. Cont.





**Figure 1.** The change in EDTA-extractable Cd (*EDTA-Cd*, %) in five kinds of soils with incubation time (14, 30, 60, 90, and 180 d). (HN, ZJ, CQ, JL, and HB denote soils as defined in Table 1. Each column is the mean of three replicates. Vertical lines on points represent standard errors.).

### 3.2. Semi-Mechanistic Models for *EDTA-Cd*

Based on the processes of Cd precipitation/nucleation, mesopore/micropore diffusion and occlusion within organic matter, the semi-mechanistic model was applied to express the aging processes, which result in the decrease in extractability of added Cd in soils. The processes can be described using Equations (12)–(15).

$$EDTA - Cd(\%) = (1 - Y_1 - Y_2 - Y_3) \times 100\% \quad (12)$$

$$Y_1 = \frac{B}{10^{(pK^0 - pH)} + 1} \times t^{\frac{C}{T}} \quad (13)$$

$$Y_2 = 1 - \exp(-Ft) \times \operatorname{erfc}(\sqrt{Ft}) \quad (14)$$

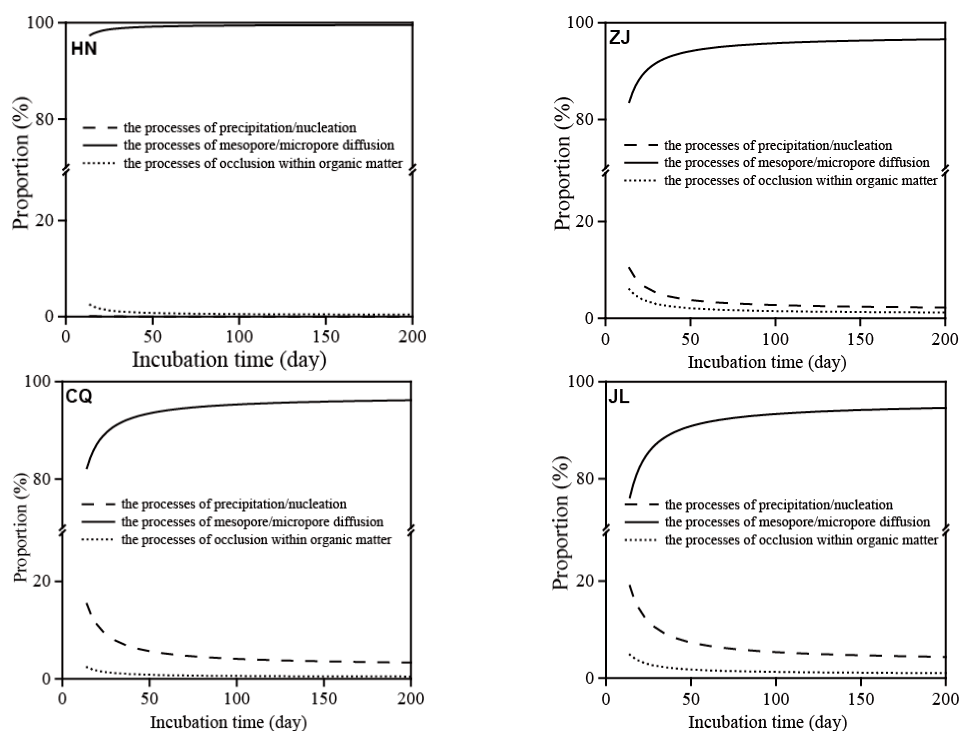
$$Y_3 = G \times \left(\frac{C_{org}}{100}\right) \times t^{H/t} \quad (15)$$

When the data were fitted by the model using the Solver function in Microsoft Excel, the parameters were subjected to the following constraints:  $B \geq 0$ ,  $C \geq 0$ ,  $F \geq 0$ ,  $D \geq 0$ ,  $G \geq 0$  and  $H \geq 0$ , with 0.000001 precision, 5% tolerance and 0.0001 convergence. The concentrations of Cd in soil solution differed because three different doses of Cd (0.6, 1.2 and 2.4 mg kg<sup>-1</sup>) were added to soils, and affected the processes of precipitation/nucleation, diffusion, and occlusion within organic matter, thereby affecting the extractability of added Cd (*EDTA-Cd*, %). Separately analyzed data of the different three doses of addition, and the parameters in the models are shown in Table 2. The root-mean-square error (RMSE) was very small and the regression coefficients (adjusted  $R^2$ ) for the semi-mechanistic models were in the range of 0.83–0.92. The values of  $pK^0$  in the models were calculated as 6.81–7.26 depending on the dose of Cd added, which were lower than those of 9.1–10.1 reported for Cd hydrolysis in water [47–49]. This is likely because the hydrolysis of Cd ions in soils were promoted by soil solid surfaces [30].

**Table 2.** Model parameters, regression coefficients (adjusted  $R^2$ ), and root-mean-square error (RMSE) derived from five soils at three added Cd concentrations.

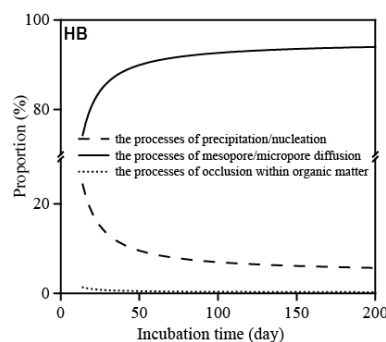
| Cd Concentration (mg kg <sup>-1</sup> ) | B    | C    | pK <sup>0</sup> | F    | G    | H     | R <sup>2</sup> | RMSE |
|---|------|------|-----------------|------|------|-------|----------------|------|
| 0.6                                     | 0.05 | 8.25 | 7.04            | 0.10 | 0.35 | 8.70  | 0.83           | 0.02 |
| 1.2                                     | 0.07 | 6.31 | 6.81            | 0.10 | 1.03 | 3.94  | 0.87           | 0.01 |
| 2.4                                     | 0.05 | 6.67 | 7.26            | 0.17 | 0.20 | 13.38 | 0.92           | 0.01 |
| 0.6, 1.2 and 2.4                        | 0.05 | 7.18 | 7.03            | 0.12 | 0.49 | 7.88  | 0.84           | 0.01 |

According to the parameters estimated by the models using the Solver function in Microsoft Excel, we calculated the respective proportions of the processes of precipitation/nucleation, diffusion and occlusion within organic matter to the changes of non-EDTA-extractable Cd (*non-EDTA-Cd*, %) incubated for different times in the five soils (Figure 2). The proportions of the processes were variation in five soils with different soil pH and OC. The decrease in *EDTA-Cd* (%) due to the processes of diffusion reached 77.3% in HB soils with pH 7.81 after incubation for 14 d, and the proportion slightly increased with increasing incubation time. While the proportion of the processes of diffusion reached 97.1% in HN soils with pH 4.54 after incubation for 14 d. Overall, however, diffusion was the predominant process leading to decreases in *EDTA-Cd* (%) in the five soils with soil pH range from 4.54 to 7.81. The processes of diffusion were slow aging processes. Almås et al. [50] also found that the transfer of Cd from solution to stable forms were significantly slower processes. The slow processes were due to inner-sphere surface complexation via partial or complete dehydration of surface species [12]. However, the processes of precipitation/nucleation and occlusion within organic matter occurred quickly. The proportions of precipitation/nucleation and occlusion within organic matter to *non-EDTA-Cd* were only 0.03–21.0% and 0.41–6.95%, respectively. Tang et al. [14] reported that in the four months aging process under unsaturated conditions, occlusion could not be an dominant factor, as revealed by the result that organically bound Cd were only in the range of 0.25–0.72% of the total Cd.



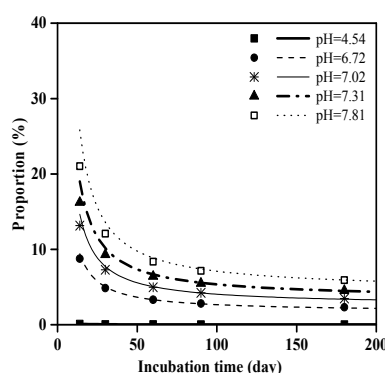
**Figure 2.** Cont.





**Figure 2.** The proportion of the processes of precipitation/nucleation, diffusion and occlusion within organic matter to the non-EDTA-extractable Cd (*non-EDTA-Cd*, %) in the Cd added and incubated for different times in five soils. (HN, ZJ, CQ, JL, and HB denote soils as defined in Table 1. The curves were predicted by the semi-mechanistic model.).

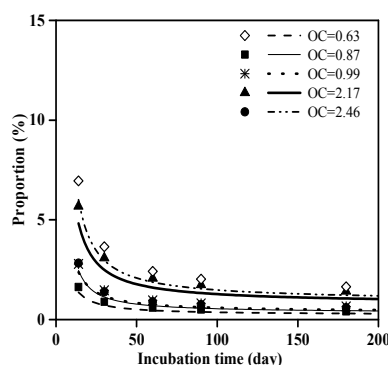
Soil pH is often known as the master soil variable. The primary influence of pH is on the metals activity and distribution between the soil solution and solid phases, such as, the precipitation and dissolution of metal solid phases, complexation and acid–base reactions of metal species, and metal sorption [26,51,52]. The direct effect of pH is on Cd fractions in soil [53–55]. Diffusion is a process driven by concentration gradients (and temperature) [16], and in the semi-mechanistic model, any influence of pH on diffusion of Cd into micropores was ignored. Crout et al. [11] similarly proposed that the rate at which a metal approaches equilibrium is independent of pH, and the metal ions are likely to undergo a process of time-dependent fixation by further reaction with the soil solid phases, although the equilibrium distribution of metal between labile and non-labile is pH dependent. However, precipitation/nucleation processes and soil pH influence the diffusion processes by controlling the Cd species present on solid surfaces and the amount of diffusible Cd in soil solution. The relationship between pH and the proportion of precipitation/nucleation to the *non-EDTA-Cd* with different incubation times is shown in Figure 3. With increasing soil pH, greater precipitation/nucleation occurred; and processes of precipitation/nucleation in the acidic red soil (pH 4.54) were almost absent. After soluble Cd had been added for 14 d, the proportion of precipitation/nucleation to the non-extractable added Cd ranged from 0.1% to 21.0% (mean 11.9%) in the five soils with different pHs in the range of 4.54–7.81. With increasing incubation time, the proportion of precipitation/nucleation to the *non-EDTA-Cd* gradually decreased.



**Figure 3.** The proportions of the processes of precipitation/nucleation to the non-EDTA-extractable Cd (*non-EDTA-Cd*, %) as a function of soil pH and incubation time (d). The curves were predicted by the semi-mechanistic model.

Soil organic matter is a predominant contributor to the pH-dependent negative charge in soils, which results in the ability to retain cationic metals of soils, leading to decrease Cd concentration [14,56].

The relationship between OC and the proportion of occlusion within organic matter to the *non-EDTA-Cd* in these soils, for different incubation times, is shown in Figure 4. With increased soil OC, there was greater occlusion within organic matter. After soluble Cd had been added for 14 d, the percentage of occlusion within organic matter to the *non-EDTA-Cd* ranged from 1.63% to 6.95% (mean 3.98%) in the five soils with different OC contents (%) in the range of 0.63–2.46%. With increasing incubation time, the proportion of occlusion within organic matter to non-extractable added Cd gradually decreased.

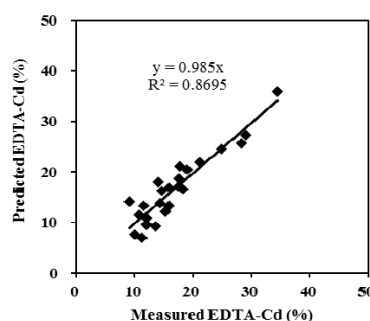


**Figure 4.** The proportions of the processes of occlusion within organic matter to the non-EDTA-extractable Cd (*non-EDTA-Cd*, %) as a function of organic carbon (OC, %) and incubation time (d). (The curves were predicted by the semi-mechanistic model.).

### 3.3. Model Validation

The measured *EDTA-Cd* (%) from incubated soils were in good accord with those predicted by the semi-mechanistic models (predicted *EDTA-Cd*, %) (Figure 5). The differences between the predicted and measured *EDTA-Cd* were <10% (range 0.01–7.7%, 2.4% on average), except for the red soil incubated for 14 d with 2.4 mg kg<sup>−1</sup> Cd added. However, the predictive power of this semi-mechanistic model (based only on pH, OC and incubation time) was satisfactory.

A limitation of the models is that one aging period was applied for the evaluation, also some Cd additions in the field often take place repeatedly with time. The present results are based on the behavior of soils under controlled laboratory conditions, and caution should be taken if the model needs to be used to the field situations. Specific factors, such as soil moisture status, microbial activities, temperature and plant absorption that would influence the extractability of Cd, were not included in this model, that may change in the field and may affect the rate of aging. Moreover, if Cd was added to soils in other forms (such as organic manure, mining waste, and sewage sludge), the model is less likely to accurately predict the aging processes of Cd, because different sources of Cd, owing to matrix effects, will most likely have different fates and exhibit different behavior.



**Figure 5.** The measured *EDTA-Cd* (%) of added Cd versus the predicted *EDTA-Cd* (%) estimated by the semi-mechanistic model at different times in five soils with three concentrations (0.6, 1.2, and 2.4 mg kg<sup>−1</sup>) of added Cd.

### 3.4. Practical Implications

The semi-mechanistic models based on aging processes for the extractability of Cd changes over time after the soluble Cd added to soils are of significance in practice, because the bioavailability and reversibility of Cd added to soils depend on the different aging processes. In the present study, the EDTA-extractable Cd was most likely controlled by the processes of diffusion and precipitation/nucleation, which means soil pH and aging time are important factors to affect the Cd extractability although OC have little effect. In practice, increasing soil pH—such as liming—may promote the processes of diffusion and precipitation/nucleation, meanwhile immobilizing Cd probably because of formation of poorly-ordered oxides and/or carbonates [57]. Also, if Cd aged due to precipitation/nucleation, Cd will be reversed and mobilized when soil acidification; if Cd aged due to micropore diffusion, the diffused Cd will also be reversed back depending time and Cd concentration/activity gradient. Furthermore, the role of aging for risk assessment and environment criteria of Cd in soil was no longer disregarded [32,57,58]. Also, the semi-mechanistic models are more robust than the aging factor, and they can be used to scale ecotoxicological data generated in short term studies to longer aging times, such as from 14 days to 1 year. Rational risk assessment and environment criteria of Cd in soil will be helpful for sustainability assessment for agricultural soils. For water-soluble Cd added to soil, the aging will lead to a decrease in EDTA-extractable Cd in soil from 0.44% to 27.95%. However, for airborne Cd from anthropogenic sources, the reactive fraction was not statistically significant between spiked soils aged for 0.5–2.5 years [57]. So that when sustainability for agricultural soils is assessed, the difference sources of Cd entering into soils and reversion processes of aging should be considered in case that sustainability assessment for agricultural soils will be under- and over-estimated.

## 4. Conclusions

The concentrations of EDTA-extractable Cd in soils initially decreased when water-soluble Cd was added to soils, and then continued to decrease over time at a slower rate. Soil pH, OC, and incubation time were key parameters controlling the aging processes. Based on Cd precipitation/nucleation on soil surfaces, mesopore/micropore diffusion, and occlusion within organic matter, a semi-mechanistic model was developed. The extractability of Cd was most likely controlled by the processes of diffusion, with precipitation/nucleation and occlusion within organic matter having far less effect, and occurred over a short time. The proportions of the processes of precipitation/nucleation and occlusion within organic matter to the non-EDTA-extractable Cd added to soils were only 0.03–21.0% and 0.41–6.95%, respectively. The measured EDTA-extractable Cd from incubated soils were in good agreement with those predicted by the semi-mechanistic model ( $R^2 = 0.829$ ), and the model was successfully validated using five largely different soils incubated for 180 d. During the soil risk assessment, the semi-mechanistic model could potentially be applied to scale ecotoxicological data obtained from different soils with different aging times.

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