The Response of Cd Chemical Fractions to Moisture Conditions and Incubation Time in Arable Land Soil

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Abstract: Heavy metal pollution in soils is an issue of global concern, and many scholars have focused on Cadmium (Cd) because of its strong biological migration and toxicity. This study explored arable land soil, changes in external Cd contamination processes and its response to soil moisture conditions, and indoor simulation. After adding an external source of 5 mg/kg d.w., the distribution of soil Cd fractions content, EXC-Cd, CAB-Cd, FMO-Cd, OM-Cd, and RES-Cd, were continuously monitored under different water management regimes, and correlation analysis and regression equations were calculated. The results show that after external Cd entered arable land soils, the binging strength of pollutants and soil gradually increased with incubation time, and the distribution of Cd chemical forms was more stable under different water management regimes. The oversaturated water content promotes the transformation of EXC-Cd to other forms. The transformation of CAB-Cd fractions can be accelerated to other fractions by field capacity, and the active conversion period was 30–60 d. Not all Cd fractions correlated between each other, under the four water management regimes, but it seems that the reducibility of the soil environment was more conducive to external Cd fixation and stability. The response surface design method (RSM) was used to establish quantitative regimes between Cd fractions with incubation time and soil moisture, and the soil moisture content and incubation time had an obvious effect on FMO-Cd content, with $R^2 = 0.9542$.

Keywords: cadmium; bioavailability; moisture conditions; arable land

1. Introduction

Soil heavy metal pollution is a global environmental problem [1]. Cadmium (Cd) and its compounds have greater mobility and biological toxicity compared to other heavy metals [2,3]. It easily accumulates in the human body, and, in Japan, itai-itai disease has appeared due to Cd poisoning [4]. The International Cancer Research Institution (IARC) classifies Cd as a human carcinogen; the EU lists Cd as a highly hazardous toxic substance, which is under regulation [5]. A National Communique on Soil Pollution Survey Bulletin, issued in April 2014, found serious Cd pollution in the soil around non-ferrous-metal mining areas. Areas exceeding the standard rate of pollution reached 7.0% in China [6]. Therefore, it is urgent to study the effects of soil Cd pollution and its key influencing factors, to ensure land safety.

The biological toxicity, migration characteristics, and environmental effects of Cd in soil depend on not only speciation but also availability and mobility [7]. Soil is a complex multi-media multi-interface environment. After external Cd enters the soil, incorporation
of Cd into the soil depends on the soil physical and chemical properties, human factors, mineral composition of the soil, and microbial activity [8]. Thus, the Cd chemical fractions are an effective way to reflect its behavioral characteristics and soil environmental effects, which can aid in understanding dispersion and enrichment as well as migration conversion regularity in soil.

Soil physical and chemical properties as well as environmental factors have an important impact on the chemical fractions and bioavailability of Cd, and the migration transformation of water management controls is the focus of much research. Soil type, redox, organic matter content, etc., can affect the distribution of Cd fractions [9]. Water management includes agricultural measures that are low cost, green, environmentally friendly, and easy to institute. Any modification of the soil water content will affect soil pH, Eh, and sulfur oxidation-reduction state changes, and can, also, affect the distribution of soil microbial species and the decomposition of organic matter. In turn, the fractions and biological effectiveness of Cd are impacted [10]. Studies have shown that when soil water saturation increases, the acid paddy soil pH increases, the Eh is lowered, and the soil reducibility is enhanced. The extracted Cd\textsuperscript{2+} content is reduced because it forms precipitates with S\textsuperscript{2−} and OH\textsuperscript{−}-oriented resection ions [11,12]. The retention time of soil water content, also, plays a vital role in this process, and when the acid paddy soil is in an aerobic state, the bioavailable content of soil Cd will increase [13,14]. However, for different kinds of soil, an increase or decrease in Cd biological extractability may also occur under soil water saturation, so the conditions and influencing factors still need to be described.

In China, the land area contaminated by Cd is around $2 \times 10^{13}$ m\(^2\), of which 1.4\% is arable land [15,16]. To explore the changes in external Cd chemical and the response of environmental factors, Cd in various forms was determined under different water management simulations, such as maintaining field water capacity, alternating dry and wet, 65\% field capacity, and long-term flooding. This study had the following goals: (1) to explore the effects of incubation time and field water capacity on the characteristics of external Cd, (2) to clarify changes in Cd chemical fractions with incubation time and water management, and (3) to identify the correlations and quantitative relationships between Cd chemical fractions and incubation time and water management. This research can provide information for developing arable land management practices and regulating Cd biotoxicity.

2. Materials and Methods

2.1. Test Soil

Testing was conducted in 2020 at the Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources. The test soil was collected from 0–20 cm topsoil in the Tongguan mining area, Shaanxi Province (110°21′40″ E, 34°30′16″ N). The sundries in soil were first removed, and, then, soil samples were air dried and run through a 2.0 mm nylon sieve, before analog testing. The field water capacity of test soil was measured, according to soil testing part 22: cutting ring methods for determination of field water-holding capacity in soil (NY/T 1121.22-2010) [17]. The basic physical and chemical characteristics of the test soil are shown in Table 1.

| pH  | Conductivity (dS·m\(^{-1}\)) | Organic Matter (g·kg\(^{-1}\)) | CEC (cmol·kg\(^{-1}\)) | Total Iron (mg·kg\(^{-1}\)) | CaCO\(_3\) (%) | Field Water Capacity (%) | Cd (mg·kg\(^{-1}\)) |
|-----|-----------------------------|-----------------------------|-------------------------|----------------------------|----------------|--------------------------|----------------|
| 9.15 | 0.367                        | 5.73                        | 3.69                    | 1.23                       | 10.72         | 21                       | 0.46           |

2.2. Materials and Experimental Design

According to the soil environmental quality standard for soil pollution risk control of agricultural lands (GB 15618-2018) [18], the control value of soil Cd pollution risk in
agricultural lands (pH > 7.5) was 4 mg/kg d.w., while 5 mg/kg d.w. was set as the target content of contaminated soil. Contaminated soil was prepared by spraying it with a CdCl$_2$ solution, and initial soil Cd content was considered as actual content. The test treatments were called GT1, GT2, GT3, and GT4, and the corresponding codes are given in Table 2. Using a weighing method, the corresponding water management regimes were field capacity, alternating wet and dry, 65% of field capacity, and saturated water content. The sampling times were 0 d, 7 d, 15 d, 30 d, 60 d, 90 d, and 120 d, and the addition of Cd was made before the first sampling. To simulate changes in the formation and biotoxicity of external Cd in arable land soil, the distribution fractions characteristics of Cd, such as exchangeable form (EXC), carbonate form (CAB), Fe-Mn oxide form (FMO), organic form (OM), and residual fraction (RES), were dynamically monitored. The simulation experiments were carried out in 500 mL plastic beakers. Four hundred grams of test soil (with an accuracy of one hundredth) were placed into each beaker. Three repetitions were set for each treatment. The test design and measured Cd contents in polluted soil are shown in Table 2.

Table 2. Test design and measured Cd content in polluted soil (mean ± SE).

| Treatment | Water Management                          | Target Content (mg/kg d.w.) | Measured Content (mg/kg d.w.) | Sampling Time (Days) |
|-----------|------------------------------------------|-------------------------------|-------------------------------|----------------------|
| GT1       | Field capacity                            | 5.0                           | 5.63 ± 0.296                 | 0, 7, 15, 30, 60, 90, 120 |
| GT2       | Alternating wet and dry                   |                               |                               |                      |
| GT3       | 65% of field capacity                     |                               |                               |                      |
| GT4       | Oversaturated water content               |                               |                               |                      |

2.3. Indexes and Methods for Determination

2.3.1. Experimental Methods

All experiments were carried out in a constant temperature incubator (DHP-9272, China), at 20 ± 0.5 °C during the 120 days. The experimental methods for the four different water management regimes were as follows:

(1) Field capacity. The water content in the basin was kept at field capacity, by adding deionized water to supplement moisture due to evaporation loss every day.

(2) Alternating wet and dry. The initial water content was set to saturated, and when the soil moisture dried in 30 days, deionized water was added until saturated and cycled again.

(3) 65% of field capacity. The water content in the basin was kept to about 65% of the field capacity.

(4) Long-term flooding. The water content in the basin was kept at oversaturated, and the water was about 5 cm above the soil surface.

2.3.2. Treatment and Determination of Soil Samples

(1) Soil in the beaker was fully mixed before sampling, and 30.0 g of sample were taken each time. To prevent the sample changes from drying, fresh soil samples were used for continuous extraction. Soil water content was measured at the same time, and Cd chemical fractions contents were calculated based on dry weight. A modified five-step Tessier continuous extraction method was used to determine the Cd chemical fractions contents [7,19].

(2) An acidometer (pHS-3C, China) was used to determine soil pH:water (v/v = 1:2.5). Microwave digestion was used for pretreatment, and, then, soil extracts were diluted after filtering (0.45 µm PTFE) before the concentrations of RES-Cd and total Cd determination were analyzed [20]. Cd chemical fractions concentrations in the soil extracts were determined using an AAS Zeenit 700 P atomic absorption spectrometer. The accuracy of the analytical procedure adopted for atomic absorption spectrometer analysis was checked by running standard solutions every 20 samples. In addition,
to control the experimental data error, the total number of chemical Cd forms was compared with the total measured Cd concentrations, and the deviation should not exceed 13%. Only excellent grade reagents were used for testing, with strict quality control [21].

2.4. Method for Coefficient Evaluation

The biological effective coefficient (BEC) was calculated using Equation (1):

\[
BEC(\%) = \frac{C_1 + C_2}{\sum_{i=1}^{k} C_i}
\]

In the formula, \( k \) is the total number of steps extracted, so \( k = 5 \). \( i \) is the extraction order, 1 EXC-Cd, 2 CAB-Cd, 3 FMO-Cd, 4 OM-Cd, and 5 RES-Cd. \( C_i \) is the extracted content of the \( i \)th step (mg kg\(^{-1}\)).

The reduced partition index (\( I_R \)) [22] was calculated using Equation (2) and describes the binding strength between heavy metals and soils. A higher-strength coefficient value indicates a closer binding strength between heavy metals and soils.

\[
I_R = \frac{\sum_{i=1}^{k} (F_i \times n^i)}{k^n}
\]

In the formula, \( F_i \) is the ratio of the content of the \( i \)th step and the total amount in the soil. \( n \) is an integer, with a value of 2.

The redistribution coefficient (\( U_{fi} \)) [23] was calculated following Equation (3).

\[
U_{fi} = \frac{F_i}{F_{ci}}
\]

In the formula, \( F_{ci} \) is the ratio of the content of the \( i \)th step and the total amount in soil before the addition of Cd.

The total redistribution coefficient (\( U_{ts} \)) is used to assess the distribution of various forms of heavy metal pollution in soil, compared to in uncontaminated soil. \( U_{ts} \) was calculated following Equation (4).

\[
U_{ts} = \sum_{i=1}^{k} (F_i \times U_{fi})
\]

Since the \( U_{ts} \) of clean soil is 1, a smaller difference between \( U_{ts} \) for contaminated soil and 1 means a more stable heavy metals distribution.

2.5. Statistical Methods

Correlation analysis, ANOVA testing, and LSD multiple comparisons were performed at the 95% significance level, using SPSS 22 (IBM SPSS Statistics, Version 22). One-way ANOVA was used to reveal the effects of different incubation times on the soil Cd fractions distribution and biological effective state changes in arable land soil. Least Significance Difference (LSD) testing was used to test the significance of each index across different treatment groups (\( p < 0.05 \)). Pearson correlation analysis (two-tailed) was used to reveal the correlation relationship between Cd fractions and incubation time and water management regimes. All figures in this paper were created using ORIGIN PRO 2021 (OriginLab Corp., Northampton, MA, USA). Response Surface Methodology (RSM) was used to establish the relationships between Cd chemical fractions, incubation time, and soil properties.

3. Results and Discussion

3.1. The Characteristics of Changes with Incubation Time under GT1

3.1.1. Soil Cd Fractions Distribution and Changes in Arable Land Soil

The movement of Cd, into the different soil fraction with incubation time in arable land soil under GT1, are shown in Figure 1. After external Cd entered the soil, adsorption-
desorption occurred between Cd and the soil particles. Further, the soil Cd fractions conversion, migration, and returning occurred in the soil environment. EXC-Cd can be present in a soil solution and hindered from conversion to other forms by soil particles [24]. Between 0 d and 7 d, the increase in EXC-Cd is, approximately, equal to the decrease in CAB-Cd, so it seems that part of the CAB fraction moved to the EXC fraction. The CAB fraction decreased slowly from 0 to 30 d, after which it decreased more drastically (at 60 d), remaining stable after. The big decrease seems to be related to the migration of part of this fraction into the FMO fraction (and slightly to the EXC fraction). The percentage of the RES and OM fractions is very low, and the increment of the percentage is less than 1%.

![Figure 1](image-url)

**Figure 1.** The movement of Cd into the different soil fractions, with incubation time in arable land soil under GT1.

The Cd fractions changes, with incubation time in arable land soil under GT1, are shown in Figure 2. After 30 days, the CAB-Cd conversion rate to FMO-Cd and OM-Cd was high, resulting in a large decrease in the CAB-Cd content. This finding was consistent with the experimental results of Lu et al.; that is, as the incubation time increased, Cd slowly converted from the exchangeable state to other forms [25]. The amount of CAB-Cd was always high during incubation, due to the alkaline soil and higher soil calcium content [26].

### 3.1.2. Changes to the Cd Biological Effective Coefficient in Arable Land under GT1

Heavy metal distribution characteristics can help evaluate their potential migration capacity and biological availability [27]. Bioavailability usually has a strong correlation with bioavailability, which is an important indicator of bioavailability. The binding strength of EXC-Cd, CAB-Cd, and soil were weak; therefore, these two forms easily migrated with higher bioavailability and potential risk. The ratio of total EXC-Cd, CAB-Cd, and total Cd content is, commonly, used to evaluate Cd availability. After external Cd entered the soil in the initial stage, it mainly existed as both EXC-Cd and CAB-Cd. Under GT1, the BEC remained stable from 0 d to 7 d, then decreased significantly from 7 d to 15 d and remained stable until 30 d, after which it decreased significantly from 30 d to 120 d (Figure 3). The biological effectiveness coefficients decreased from 90.1% to 61.5%, by nearly 30%. During the incubation time of 30–60 d, the bioeffective state declined, by up to 16.2%. This result further confirms that the bioavailability decreases with the incubation proceed, and the pollutants exist in a more stable way [28]. The transformation of CAB-Cd
to other forms, especially FMO-Cd, is the reason for the reduction in the bioavailability of Cd [29]. Obviously, Cd with lower bioavailability and mobility is more difficult to be exposed to the recipient population through the migration and transformation, with a lower environmental risk [30].

**Figure 2.** The Cd fractions changes, with incubation time in arable land soil under GT1. Data shown are means ± standard error (n = 3), and different letters (a, b, c, d) present significant differences between time points of the same Cd fraction at p < 0.05.

**Figure 3.** Change in the bioavailability coefficient of Cd, with incubation time in arable land soil under GT1. Data shown are means ± standard error (n = 3), and different letters (a, b, c, d, e) present significant difference at p < 0.05.
3.2. The Characteristics of Cd Fractions Changes with Incubation Time

Water management regimes can change soil redox properties, affecting the physical chemistry of external heavy metals that further migrate and transform biological effectiveness [31,32]. The change characteristics of Cd fractions over different incubation times were analyzed by simulating different water management regimes. The formation of soil oxidative reduction properties was affected by the water management model. The various forms, distributions, conversions, and migrations were analyzed under different water management regimes.

Changes in Cd chemical forms, under four different water management regimes and incubation times, are shown in Figure 4. The incubation experiment was carried out under water management regimes. Through continuous monitoring of the chemical forms of contaminated horizontal external Cd in arable land soil (up to 120 d), we found that different water management conditions resulted in different Cd chemical forms.

The EXC-Cd (Figure 4a) content changes are different across the four water management regimes. Under GT1, no modification in EXC-Cd content was observed, only the EXC-Cd content at 120 d decreased significantly compared with the incubation time at 15 d and 30 d. Under GT2, EXC-Cd increased from 0 d to 7 d, then remained stable until 30 d, after which it decreased significantly from 30 d to 60 d and was 23.74% less than the samples at 30 d; next, it increased and decreased again. Under GT3, the EXC-Cd content decreased from 0–7 d, and, then, it increased until 15 d, after which it decreased significantly from 15–60 d, and, finally, EXC-Cd remained relatively stable and did not decrease with an extension of incubation time from 60–120 d. Under GT4, the EXC-Cd content decreased from 0–7 d, and, then, it remained relatively stable until 30 d, before decreasing significantly from 30–60 d. It was relatively stable from 60–90 d, then further decreased from 90 d to 120 d.

Except under GT1, EXC-Cd content decreased greatly from 30–60 d under the remaining water management regimes, which was the active period of EXC-Cd conversion to other forms. In order to see the effect of the different water régime on Cd fractions, a statistical comparison has been done between the treatments within each sampling time. Under GT2 and GT3, EXC-Cd content was always greater than under GT1 and GT4 from 7–120 d, EXC-Cd content under GT1 was always the lowest from 0–30 d, and EXC-Cd content under GT4 was always the lowest from 60–120 d. It seems that a higher soil water content promotes the transformation of EXC-Cd to other forms. The change trend of EXC-Cd fraction during 60–120 d is consistent with Xu et al. [33]: the continuous flooding has shown the lowest content of soil EXC-Cd than the other treatments.

For CAB-Cd (Figure 4b), under GT1, the CAB-Cd content was relatively stable from 0–30 d. It was reduced by 63.06% during 30–60 d. Afterwards, the content remained relatively stable. Under GT2, CAB-Cd content at 7 d, 30 d, 60 d, 90 d, and 120 d was significantly lower compared to content at 0 d. CAB-Cd content declined greatly during 30–60 d and was reduced by 44.79%. Under GT3, CAB-Cd content at 7 d, 30 d, and 120 d was significantly lower compared to content at 0 d ($p < 0.05$). CAB-Cd content was relatively stable from 0–30 d, and, then, it gradually decreases as incubation time increased from 30–60 d, before stabilizing. Under GT4, no modification in CAB-Cd content was observed, so only the CAB-Cd content at 60 d was significantly higher, compared to the content at 7 d and 15 d. The statistical comparison result showed high levels of CAB-Cd content from 0–30 d under GT1. CAB-Cd content was always greater under GT4 than other water management regimes, and CAB-Cd content was the lowest from 60–120 d under GT1. CAB-Cd content decreased greatly from 30–60 d under the remaining water management regimes under GT1, which was the active period of CAB-Cd conversion to other fractions.

Field water capacity, or the increase in soil water content, can accelerate the transformation of external Cd to more stable forms in the soils [30]. Results also suggested that the water regimes significantly determine the effective risk of extractable fractions [34].

Under the different treatments, FMO-Cd (Figure 4c) content increased rapidly from 15–90 d, and the maximum value was reached at 90 d or 120 d. Under GT1, the FMO-Cd content increased from 0–90 d, with a maximum value at 90 d. After that, the content was
relatively stable, and it increased 2.91 times compared to the initial content. Under GT2, the FMO-Cd content reached a maximum at 120 d, and the content increased by 2.63 times compared to the initial content. Under GT3, the FMO-Cd content reached a maximum at 120 d, and the content increased by 3.35 times compared to the initial content. Under GT4, FMO-Cd content was significantly different ($p < 0.05$) compared with the incubation time from 15–90 d, and was 4.55 times higher than the initial content. In both water management regimes for GT1 and GT4, FMO-Cd was converted more from other forms compared to GT2 and GT3, indicating that high soil water content or stronger reducibility is conducive to the transformation of FMO-Cd. The statistical comparison result showed that FMO-Cd content was always the lowest under GT4 than other water management regimes from 0–60 d, and, then, it increases from 60–90 d; after that, FMO-Cd content was relatively stable until 120 d. The result confirms that the contents of FMO fraction were higher in the dry–wet cycling area [35]. There was high conversion capacity that resulted in a low existing state, so the reduction in the oversaturation environment was more conducive to external Cd fixation and stability [36].

OM-Cd and RES-Cd (Figure 4d,e) were the least proportional of the five forms, with the sum of the two contents accounting for about 2.73–3.91% of the total. Under GT1, the OM-Cd fraction remained stable from 0–15 d, increasing slowly from 15 d to 30 d, after which it remained stable again. Under GT2, the OM-Cd fraction remained stable from 0–30 d, increasing rapidly until 60 d, after which it remained stable again, reaching a maximum at 120 d, with a content increase of 2.00 times compared to the initial content. Under GT3, the OM-Cd fraction remained stable from 0–15 d, increasing until 30 d, after which it remained stable again, reaching a maximum at 120 d, with a content increase of 1.77 times compared to the initial content. Under GT4, the OM-Cd fraction remained stable from 0–15 d, increasing until 30 d, after which it remained stable from 30–60 d, again increasing from 60–90 d, and, then, it decreased slightly.

Under GT1, the RES-Cd fraction increased from 0–7 d and decreased from 7–15 d, then, it increased again until 60 d, after which it remained stable, reaching the maximum value 90 d, with a content increase of 2.56 times compared to the initial content. Under GT2, the RES-Cd fraction remained stable from 0–30 d, increasing from 30–60 d, after which it remained stable, again. Under GT3, the RES-Cd fraction increased from 0–7 d, and it remained stable until 120 d, so only the RES-Cd content at 120 d reached significant levels compared with the incubation time at 30 d. Under GT4, the RES-Cd fraction remained stable from 0–15 d, increasing rapidly from 30–60 d, and, then, it remained stable until 120 d, so the RES-Cd content at 30 d, 60 d, 90 d, and 120 d reached significant levels compared with the incubation time at 0 d, which was significantly higher compared to content at 0 d, reaching a maximum at 120 d, about 0.634 times the initial content.

Figure 4. Cont.
Figure 4. Cont.
After external Cd enters the soil, the binding strength of pollutants and soil gradually increased with incubation time, and the distribution of Cd chemical forms was more stable under different water management regimes. The soil binding strength coefficient ($I_R$) and the total redistribution coefficient ($U_{ts}$) of the external Cd of the initial and end stages under different water management regimes are shown in Figure 5. Under GT1, $I_R$ increased by 50.76% from the initial stage, and $U_{ts}$ decreased by 9.41%. Under GT2, $I_R$ increased by 45.00% from the initial stage, and $U_{ts}$ decreased by 19.94%. Under GT3, $I_R$ increased by
81.61% from the initial stage, and $U_{ts}$ decreased by 11.74%. Under GT4, $I_R$ and $U_{ts}$ reached their maximum respective values of 103.29% and −34.86%, compared with GT1, GT2, and GT3. When the soil was always in the reduction environment, the rate of external Cd transformation to forms that were difficult to extract was at a maximum. In addition to the GT4 treatment, the increases and decreases in $I_R$ and $U_{ts}$ were inconsistent. Under GT2 and GT1, the $I_R$ increase was about the same, being 60.77–129.56% of the increase under GT3 and GT4. The reduction in $U_{ts}$ was, basically, the same under GT1 and GT3 conditions, which was 69.90–270.37% of GT2 and GT4. This indicated that under the same incubation time, the chemical form stability conversion rate of external Cd was low, and the formal stability was longer than other treatments in GT1.

![Graph](image)

**Figure 5.** $I_R$ and $U_{ts}$ changes under different water management regimes in arable land soil.

3.4. Correlation and Quantitative Relationship between Cd Fractions and Incubation Time as well as Water Management Model

3.4.1. Correlation Analysis of Cd Fractions and Incubation Time as well as Soil Water Content

A correlation analysis of quantitative data can show the relationship between factors and how strong it is. Data such as soil moisture, incubation time, and Cd chemical forms were analyzed using SPSS 22.0, and the results are shown in Figure 6. It can be seen that EXC-Cd fraction was extremely significantly negatively correlated with FMO-Cd (−0.58) and RES-Cd (−0.39), and was significantly negatively related to OM-Cd (−0.24). The CAB-Cd fraction was extremely significant negatively correlated with FMO-Cd (−0.62), OM-Cd (−0.46), and RES-Cd (−0.41), while EXC-Cd content increases, FMO-Cd and RES-Cd contents decrease, and Cd moves from the FMO-Cd and RES-Cd fractions to the EXC-Cd fraction. Similarly, CAB-Cd content increases, FMO-Cd, OM-Cd, and RES-Cd contents decrease, and Cd moves from the FMO-Cd, OM-Cd and RES-Cd fractions to the CAB-Cd fraction. As EXC-Cd and CAB-Cd contents decreased, FMO-Cd, OM-Cd, and RES-Cd contents gradually increased, and most of the EXC-Cd and CAB-Cd were converted to FMO-Cd. The FMO-Cd content was significantly correlated with OM-Cd (0.76) and RES-Cd (0.54). As the FMO-Cd content increased, the OM-Cd and RES-Cd contents increased, which showed that FMO-Cd played an important role for other forms in arable land soil [30]. There were no significant correlations between the Cd fractions content and soil moisture, and not all Cd forms correlated between each other. The EXC-Cd and CAB-Cd contents had extremely significant negative correlations with incubation time, while FMO-Cd, OM-Cd, and RES-Cd had extremely significant positive correlations with incubation time. As the incubation time increased, EXC-Cd and CAB-Cd fractions contents decreased, while FMO-Cd, OM-Cd, and RES-Cd increased, and the external Cd fractions tended to be more stable. The result was consistent with other studies, in which rapid reduction of bioavailable Cd was found, within 10–20 days after adding heavy metals [37]. The results are, also, documented by Fan and Zhang [38,39]: EXC-Cd and CAB-Cd fractions in soil showed a contrary pattern with RES-Cd and OM-Cd, respectively.
3.4.2. Quantitative Relationship between Formation and Incubation Time as well as Soil Water Content

The correlation analysis of Cd fractions content, soil moisture, and incubation time indicated complex relationships. To establish a quantitative relationship between the Cd chemical fractions and influencing factors, the response surface design method (RSM) was used to solve multivariate problems and establish quantitative regimes between factors and response values. This method is widely used in experimental design and data processing. In this study, the Cd fractions content data were used as a modeling sample under different processing conditions. The soil moisture content and incubation time are set as independent variables, and different Cd forms are set to establish a quantitative relationship model for Cd fractions content, soil properties (soil moisture conditions), and incubation time, as shown in Table 3.

The model showed that Cd fractions content, soil moisture content, and incubation time had a good determination coefficient. There was a high degree of fit between FMO-Cd content, soil moisture content, and incubation time, with an $R^2$ of 0.9542. This indicated that the soil moisture content and incubation time had an obvious effect on FMO-Cd content. The EXC-Cd, CAB-Cd, and OM-Cd contents, soil moisture content, and incubation time also had high degrees of fit, with $R^2$ values of 0.7846, 0.7199, and 0.7029, respectively. The RES-Cd content, soil moisture content, and incubation time had a lower degree of fit, with an $R^2$ of 0.5250. This was a very convenient way to calculate the contents of Cd chemical forms using quantitative models. The biological toxicity of Cd in soil and its stability can be estimated by monitoring soil moisture content and incubation time. Some scholars have also, obtained the prediction models for the bioavailability of cadmium. Wen et al. used a polynomial surface model to evaluate the bioavailability of Cd to rice (Oryza sativa L.) in the karst region of southwestern China, and they found that soil Ca, pH, and total Cd are the controlling factors of Cd bioavailability [40]. Six bioaccessibility prediction models for Cd, based on total Cd content, have been constructed by Zhang et al., and a prediction model was obtained with a higher correlation $R^2$, by introducing Fe mineral content ($R^2$: 0.528–0.986) [41]. In future research, on the basis of the existing prediction model, the influencing factors such as pH, Eh, and organic matter content will be introduced to further increase the correlation $R^2$, and prediction models can help accurately assess the ecological risks of Cd-contaminated soil.

Figure 6. Relationship between various fraction Cd, soil moisture, and incubation time.
Table 3. Main factors and regression equations affecting Cd fractions content.

| Content  | Factors ($x_i$)             | Quantitative Equation                                                                 | C.V. (%) | Adjusted $R^2$ |
|----------|----------------------------|--------------------------------------------------------------------------------------|----------|----------------|
| EXC-Cd ($y_1$) | incubation time ($x_1$), soil moisture ($x_2$) | $y_1 = 2.66112 + 3.21623x_2 - 3.47460 \times 10^{-3}x_1 - 0.013585x_2^2 + 8.77084 \times 10^{-6}x_1^2$ | 9.31     | 0.7846         |
| CAB-Cd ($y_2$)  | incubation time ($x_1$), soil moisture ($x_2$) | $y_2 = 2.51371 + 0.35515x_2 - 0.026703x_1 + 0.023977x_2x_1 - 3.90473x_2^2 + 2.44129 \times 10^{-5}x_1^2 + 0.016047x_2^2x_1 - 1.98107 \times 10^{-4}x_2x_1^2 + 2.36993x_2^3 + 6.61833 \times 10^{-7}x_1^3$ | 18.82    | 0.7199         |
| FMO-Cd ($y_3$)  |                                  | $y_3 = 0.35999 + 0.34994x_2 + 0.016694x_1 - 0.017412x_2x_1 - 0.071505x_2^2 + 1.04641 \times 10^{-4}x_1^2 + 3.51351 \times 10^{-3}x_2x_1 + 1.18289 \times 10^{-4}x_2x_1^2 - 0.37843x_2^3 - 1.26683 \times 10^{-6}x_1^3$ | 12.15    | 0.9542         |
| OM-Cd ($y_4$)   | incubation time ($x_1$), soil moisture ($x_2$) | $y_4 = 0.033499 + 0.09494x_2 + 1.38432 \times 10^{-3}x_1 - 2.25142 \times 10^{-4}x_2x_1 - 0.12317x_2^2 - 5.57851 \times 10^{-6}x_1^2$ | 30.98    | 0.7029         |
| RES-Cd ($y_5$)  |                                  | $y_5 = 0.037624 - 0.084365x_2 + 5.73235 \times 10^{-4}x_1 - 3.53173 \times 10^{-4}x_2x_1 + 0.25973x_2^2 - 6.66872 \times 10^{-6}x_1^2 + 2.04227 \times 10^{-4}x_2^2x_1 + 1.59355 \times 10^{-6}x_2x_1^2 - 0.17599x_2^3 + 2.69750 \times 10^{-8}x_1^3$ | 14.47    | 0.5250         |

4. Conclusions

To explain Cd changes in soil and their response to soil moisture, indoor simulation experiments were carried out. Cd was added to arable land soil using external simulation, and the dynamic changes of Cd chemical forms were monitored under different water management regimes and incubation times. Correlations and quantitative relationships between Cd chemical forms, soil moisture, and incubation time were identified. The biologically effective coefficient gradually decreased, and the refurbishment of Cd tended to stabilize, under field capacity. The binging strength of external Cd and soil gradually became more integrated, and the Cd fractions distribution was close to stable under different water management regimes. The statistical comparison result, between the different water regimes on Cd fractions within each sampling time, showed that oversaturated water content promotes the transformation of EXC-Cd to other forms. The transformation of CAb-Cd fractions can be accelerated to other fractions by field capacity, and the active conversion period was 30–60 d. Correlation analysis of quantitative data showed that the EXC-Cd fraction was extremely significantly negatively correlated with FMO-Cd and RES-Cd. The CAb-Cd fraction was extremely significant negatively correlated with FMO-Cd, OM-Cd, and RES-Cd. When the soil water regime was oversaturated water content, EXC-Cd content decreased rapidly, FMO-Cd and RES-Cd contents increased, and Cd moved from the EXC-Cd fraction to the FMO-Cd and RES-Cd fractions. Similarly, when the soil water regime was at field capacity, Cd moved from the CAb-Cd fraction to the FMO-Cd, OM-Cd, and RES-Cd fractions. The response surface design method (RSM) was used to establish the quantitative regimes between Cd fractions and incubation time and soil moisture. It is, theoretically and practically, important to reveal the migration transformation and changes of Cd fractions in soil environments. In addition, research can also provide a basis for the accurate development of soil pollution prevention and control measures.
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