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Effects of Several Organic Fertilizers on Heavy Metal Passivation in Cd-Contaminated Gray-Purple Soil

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Soil heavy metal pollution has become a major ecological and environmental problem and a serious threat to global food security. Organic fertilizer can not only improve soil quality and provide nutrients for plants but also reduce the harm of heavy metal ions to a certain extent, meaning it has become a current research hotspot in the field of heavy metal passivation. In this paper, a completely combined experimental design was used to compare the effects of five organic fertilizers [nutshell organic fertilizer (NOF), pig manure organic fertilizer (PMOF), sludge organic fertilizer (SOF), humus soil organic fertilizer (HSOF) and earthworm soil organic fertilizer (ESOF)] on available Cd in soil with different pollution levels at different dosages, and the passivation mechanism of soil Cd was preliminarily discussed. The results showed that all kinds of organic fertilizers were passivated by reducing the Cd availability, and their effects on the Cd availability of purple soil were closely related to the degree of soil pollution and the amount of organic fertilizers. The passivation effect of moderate Cd-contaminated soil was the best, which increased with the increase of organic fertilizer application rate, and the effects of NOF and SOF were the best. However, the passivation effect of organic fertilizers on soil Cd was the worst in mild Cd-contaminated soil, especially ESOF. The results of Cd morphological correlation analysis showed that Exe-Cd and FeMnOx-Cd in the soil had significantly positive contributions to available Cd, while Res-Cd showed significantly negative contributions. And in moderate Cd contaminated soil, Exe-Cd content decreased by 7.12%–28.50%, while Res-Cd content increased by 19.74%–65.81%. In addition, the content of available Cd in soil decreased first and then increased with time after adding organic fertilizer, and reached the lowest value at 15 days and stabilized after 60 days. The conclusion of this paper can provide a theoretical basis for the rational use of organic fertilizer to reduce the bioavailability of cadmium in Gray-Purple soil.

Keywords: organic fertilizer, Cd, availability, heavy metals speciation, passivation

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1 INTRODUCTION

Rapid industrial development and the extensive use of pesticides and mineral fertilizers have led to the widespread existence of heavy metals in agricultural soils. Rice is the largest food crop in China. Nearly two-thirds of the population live on rice. According to the survey, there is about 13,000 hm^2 of Cd-contaminated farmland soil in China, including 11 provinces and 25 regions (Guo and Lin, 1998;

Hou and Li, 2017). The results of the China soil pollution survey bulletin released in 2014 (CAEPI, 2014) showed that there was significant indigenous heavy metal pollution in cultivated land soil and even the whole soil in China. The heavy metal pollution of Pb, As, Ni and Cd were more serious. From the analysis of the distribution of soil pollution in China, the soil heavy metal pollution in Southern China was more serious than that in Northern China, and the large area of soil heavy metal content exceeded the standard in the Southwest and central South of China. The exceeding standard rate of Cd pollution was 7.0%, and the proportions of four different pollution levels from severe to slight pollution were 0.5%, 0.5%, 0.8%, and 5.2%, respectively (Zhang, 2002). Cd is generally released into the environment through human activities such as mining and metal ore processing (Yang et al., 2018). It has the characteristics of strong toxicity, poor mobility, and easy accumulation in soil, and is toxic even at low exposure levels (Clemens et al., 2013). A high concentration of Cd stress can induce many reactive oxygen species and malondialdehyde content in plant cells and cause the upregulation of antioxidant enzyme gene expression. Cd stress can also destroy the integrity of the photosynthetic system, inhibit photosynthesis, and reduce nutrient uptake by plants, thereby inhibiting photosynthesis and reducing the activities of several key enzymes, including superoxide dismutase (SOD), guaiacol peroxidase (POD), catalase (CAT), ascorbate peroxidase (APX) and glutathione peroxidase (GPX). (Araujo et al., 2017; Zong et al., 2017; Chandorkar et al., 2019). The transportation of Cd and other trace metals to the human body through the food chain also has great potential to harm human health (Chaney, 2015). Therefore, eliminating the influence of Cd contaminated soil on the quality and safety of agricultural products, thereby reducing its harm to human beings is an important issue related to the national economy and public health.

At present, the role of organic fertilizer in fertility improvement, soil biological activity improvement, nutrient recycling, and sustainable agricultural development has been generally confirmed (Bulluck et al., 2002; Chen et al., 2005; Sharrma et al., 2005). The organic matter and beneficial microorganisms in organic fertilizer have strong adsorption and chelating effects on heavy metal ions. The bioavailability was reduced because of the reduction of contents of water-soluble heavy metals and exchangeable heavy metals in soil. Therefore, it showed very superior properties in improving farmland productivity and repairing heavy metals. (Chen et al., 2003; Andersson and Simon, 2009; Ansari and Mahmood, 2017). The mechanism of repairing heavy metal pollution in soil by organic fertilizer is due to its material composition and properties. Organic fertilizer contains a large number of low molecular simple organic acids and even polymer humus substances and other high molecular active substances, which have complex structures and can affect the conversion process, occurrence morphology, and biological activity of heavy metals in the soil through various mechanisms, including direct complexation/adsorption of heavy metal ions (Senesi et al., 1995; Liu et al., 2008), formation of organic-inorganic complexes with soil inorganic components (Matilainen et al., 2010), as electron shuttles which affects soil redox properties (Chen et al., 2011; Jiang et al., 2015), affecting soil pH and buffering performance (Österberg et al., 1999; Martina et al., 2009). There are great differences in the composition and properties of organic fertilizers due to the different sources of organic fertilizers, composting methods, and degree of maturity. Therefore, there are also significant differences in the regulation of soil heavy metal availability (Wang et al., 2010; Qin et al., 2014). Huang et al. (2014) found that the application of cattle manure organic fertilizer could reduce exchangeable Cd and residual Cd by 28.84%–36.33% and 6.39%–19.29% respectively, and increase carbonate-bound Cd and organic-bound Cd by 10.95%–75.27% and 44.91%–68.31% respectively, which proved that organic matter could reduce the bioavailability of Cd by changing the speciation of Cd in black soil, thereby inhibiting the absorption of Cd by plants. Ma et al. (2015) showed that the application of bio-organic fertilizer with special functional microorganisms and organic compounds can reduce the available Cd and Pb in acid paddy soil by 17.36 % and 18.45%, respectively, and significantly reduce Cd and Pb contents in rice. Liu et al. (2014) found that the three organic fertilizers can reduce the Cd content in various parts of wheat through the study of sheep manure, chicken manure, and pig manure. The comprehensive effect is as follows: pig manure > sheep manure > chicken manure. Organic fertilizer reduces its bioavailability by reducing soil exchangeable and carbonate-bound Cd content, increasing iron-manganese oxidation, organic binding, and residual Cd content. However, some studies have found that the application of organic fertilizers has increased the availability of heavy metals in the soil and increased the accumulation of heavy metals in plants. Pan and Zhou (2007) found that after the application of straw organic fertilizer and pig manure organic fertilizer, the exchangeable Cd in the soil increased by 43.2 % and 17.3% compared with the application of inorganic fertilizer, respectively. The Cd content in the wheat grain also exceeded the relevant Chinese standards by 60 % and 70%, respectively. Shi et al. (2009) found that after adding humic acid, the content of water-soluble Pb in soil increased, so it is necessary to reduce the harm of Pb through the adsorption of zeolite. Ushijima et al. (2016) prepared organic materials by heat treatment of organic waste in the presence of Lewis acid catalyst. It was found that the content of Cd in alfalfa was related to the additional amount of organic materials. When the addition amount was 10%, humus may reduce the oxidative stress caused by Cd, thereby promoting the growth of alfalfa, and reducing its accumulation in plants. When the addition amount was 25%, the toxicity of Cd was dominant compared with humus fertilization, resulting in growth inhibition and higher Cd accumulation. Similarly, Wang et al. (2014) also indicated that although organic materials could reduce the effectiveness of heavy metals in soil, they did not reduce the total amount of heavy metals in soil, and the dissolved organic matter and other factors generated by the decomposition of heavy metals in organic materials may lead to the aggravation of soil heavy metal pollution and soil acidification. Therefore, the use of organic materials to repair soil there are certain environmental risks, the effect of remediation depends on the type and

TABLE 1 | Basic physicochemical properties of Manures.

Organic fertilizer type	pH (H_2O)	DOC (g/kg)	TCd (mg/kg)	Organic matter (g/kg)	TN (g/kg)	TP (g/kg)	TK (g/kg)
NOF	8.08	66.1	0.31	300.41	11.54	10.21	7.96
PMOF	8.06	100	0.23	578.95	18.56	12.69	10.44
SOF	8.1	148	0.26	473.36	16.05	13.97	15.66
HSOF	8.09	251	0.18	733.69	8.42	10.32	8.29
ESOF	8.12	90.2	0.27	367.76	15.91	14.73	9.52

composition of organic materials and soil environmental conditions. At present, the common sources of organic fertilizer in the world include livestock manure such as pigs, cattle, and chickens, plant debris such as nutshell, fruit husk, and rapeseed, organic sludge waste, and humus soil from various organic waste. There are differences in the components of various types of organic fertilizers, and the influence and regulation performance on the form of heavy metals in the soil must be different. However, there is a lack of systematic comparative study on the regulatory effect of different types of organic fertilizers and different degrees of heavy metals on the speciation effectiveness of heavy metals, which restricts the scientific application of organic fertilizers as soil heavy metal remediation materials, especially in the purple soil area of Chongqing where Cd pollution is more serious. Therefore, in this study, Cd, a heavy metal with great potential to harm public health, the environment, and cause widespread pollution was selected as the research object. Five kinds of common organic fertilizers were selected: nutshell organic fertilizer (NOF), pig manure organic fertilizer (PMOF), sludge organic fertilizer (SOF), humus soil organic fertilizer (HSOF), and earthworm soil organic fertilizer (ESOF). Through soil incubation experiment, the varying regularity of Cd availability and passivation effect of different types and different dosages of organic fertilizer on farmland soil with three different Cd pollution levels of the same soil type were studied, to provide a basis for the scientific application of organic fertilizer and soil pollution remediation.

2 MATERIALS AND METHODS

2.1 Materials

2.1.1 Organic Fertilizer

In this study, five types of organic fertilizers with wide application and large differences in incubation were selected as follows: nutshell organic fertilizer (NOF), pig manure organic fertilizer (PMOF), sludge organic fertilizer (SOF), humus soil organic fertilizer (HSOF) and earthworm soil organic fertilizer (ESOF). The five organic fertilizers were all purchased from Hebei Shi Yuan Su Fertilizer Technology Co., Ltd. and the basic physical and chemical properties are shown in **Table 1**.

2.1.2 Soil Collection, Characterization

The soil in this research is purple-brown purplish soil (GPS, the same below) widely distributed in Southwestern China, which was collected in the 0–20 cm layer from Fuling District, Chongqing, China. The gravel and plant residues were removed from the soil samples. Soil chemical parameters pH, DOC, TCd, OM, TN, TP, and TK were determined, which are presented in **Table 2**.

2.2 Experimental Methods

2.2.1 Preparation of Cd-Contaminated Soil

To accurately control the level of Cd pollution in soil, the artificial simulation of Cd-contaminated soil was carried out. After natural drying, the soil samples were milled and passed through a 2 mm standard sieve. Refer to the secondary standard (0.3 mg/kg) in the Soil Environmental Quality Standard (GB15618-1995), the air-dried and sieved soil was spiked with $CdCl_2$ to a final Cd concentration of 0, 1, 2, 5 mg/kg and wetted to 70% of its field capacity, which was recorded as Cd-0, Cd-1, Cd-2, Cd-5. The Cd-contaminated soil was incubated in dark at room temperature for 3 months for further use.

2.2.2 Organic Fertilizer Incubation Experiment

The experiment was conducted as a completely randomized design in a 4 × 5 × 3 factorial scheme, with four levels of Cd contaminated soil (Cd-0, Cd-1, Cd-2, and Cd-5), and five types of organic fertilizers (NOF, PMOF, SOF, HSOF, and ESOF), and three rates of application (2, 4, 8 g/kg), with two replications. A control treatment without organic fertilizer was added, with three replications.

Five different types of organic fertilizers were incorporated with a 500 g Cd-contaminated air-dried soil in a 1,000 mL plastic container with lids according to the three dosages, and homogeneously mixed. Deionized water was added to reach 70% field capacity. The aging process was simulated in the laboratory through an incubation experiment. Periodically during the incubation, deionized water was cautiously sprayed to bring samples back to 70% field capacity by weighting the pots. The experiment was kept in a laboratory environment with a constant temperature of 25°C. One soil sample of approximately 10 g was collected from each plastic container at 1, 7, 15, 30, 60, and 90 days of incubation for the determination of Cd speciation. Repeated sampling 3 times for all measurements.

2.3 Analysis Method

2.3.1 Basic Physical and Chemical Properties of Soil and Organic Fertilizer

The determination of soil pH, organic matter content, DOC, and other basic physical and chemical properties refer to the "Soil Agricultural Chemistry Analysis Method" (Lu, 2000). The total Cd content in the soil is digested with a mixture of aqua regia

TABLE 2 | Basic physicochemical properties of soil sample.

Soil	pH	DOC (g/kg)	TCd (mg/kg)	Organic matter (g/kg)	TN (g/kg)	TP (g/kg)	TK (g/kg)
GPS	8.15	1.59	0.02	23.42	1.24	0.73	0.81

(HNO_3: HCl = 1: 3): $HClO_4$ at a ratio of 2:1, and the Cd^{2+} in the solution after digestion is determined by flame atomic absorption spectrophotometry (TAS-900, Beijing Puxi).

2.3.2 Sequential Extraction Procedure

For the fractionation procedure, soil samples were collected from each experimental pot, air-dried, and sieved using a 2 mm sieve. Approximately 1 g of the Cd-contaminated soil treated with organic fertilizer was weighed into a 50 mL polypropylene centrifuge tube to separate copper into six operationally defined fractions, according to Tessier et al. (1979), as follows:

Fraction 1: Soluble + exchangeable Cd (Exe-Cd), extracted with 16 mL of 0.1 M $MgCl_2$.

Fraction 2: Carbonates bound Cd (Carb-Cd), extracted with 16 mL of 1 M NaAOc, at pH 5.

Fraction 3: Fe and Mn oxide bound Cd (FeMnOx-Cd), extracted with 30 mL of 0.04 M $NH_2OH{\cdot}HCl$ (hydroxylamine hydrochloride) in acetic acid, at pH 3.

Fraction 4: Organic matter strongly bound Cd (OM-Cd), extracted with 10 mL of 30% H_2O_2 at pH 2, followed by the addition of 8 mL of 3.2 M NH_4AOc in 20% HNO_3.

Fraction 5: Residual fraction (Res-Cd), extracted with 8 mL of aqua regia (HNO_3: HCl = 1: 3) and 2 mL $HClO_4$.

The available Cd content in soil was extracted and determined with 1 M CH_3COONH_4 solution. Analysis of Cd was performed by Atomic Absorption Spectrophotometry (TAS-900, Beijing Persee). The recovery rate Cd in all soil samples was higher than 90%.

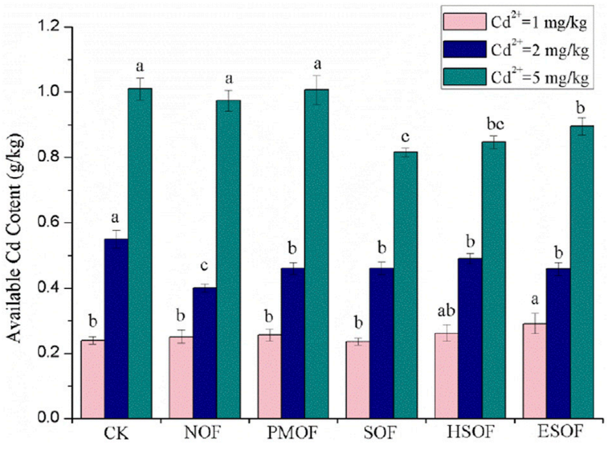

FIGURE 1 | The effect of organic fertilizer types on the contents of available Cd in soils with different Cd loads (The letter on the bar shows the statistical differences between treatments at $p < 0.05$)

2.3.3 Statistical Analysis

Microsoft Excel 2007 and Origin Pro 8.5 for data recording and preliminary analysis. Analysis of variance (ANOVA) and Tukey's multiple range tests ($p < 0.05$) were used to determine the statistical significance of the organic fertilizer treatment effects on Cd availability using the SPSS 17.0 package.

3 RESULTS

3.1 The Effect of Organic Fertilizer on the Availability of Soil Cd

3.1.1 The Effect of Organic Fertilizer Types on Available Cd in Soil With Different Cd Pollution Levels

After applying organic fertilizer to soils with different pollution levels for 90 days, the average content of available Cd in the soil is shown in **Figure 1**. It can be seen that the content of available Cd in moderate and severe Cd-contaminated soil can be reduced by organic fertilizer, and the effect of organic fertilizer on the available Cd content in the soil is related to the degree of soil pollution and the type of organic fertilizer. In moderate Cd-contaminated soil (Cd^{2+} = 2 mg/kg), all organic fertilizer treatments significantly reduced the availability of Cd in soil. Among them, NOF had the best inhibitory effect on the availability of Cd in soil, and its available Cd decreased by 27.15% compared with the control (0.55 mg/kg), and the other treatments decreased by 10.86%–16.55% compared with the control. There was no significant difference between the treatments. In severe Cd-contaminated soil (Cd^{2+} = 5 mg/kg), only SOF, HSOF, and ESOF could significantly reduce available Cd content in the soil ($p < 0.05$), which were 19.18%, 16.14%, and 11.36% lower than the control (1.01 mg/kg), respectively. For mildly Cd-contaminated soil (Cd^{2+} = 1 mg/kg), the application of organic fertilizer increased the availability of Cd in soil. Compared with the control (0.24 mg/kg), the available Cd content in five organic fertilizer treatments increased by 1.79%–21.38%, respectively, and the ESOF treatment increased the most, reaching a significant level of $p < 0.05$. Among them, SOF had the best effect.

3.1.2 The Effect of Organic Fertilizer Addition on Available Cd in Soil With Different Cd Pollution Levels

Figure 2 shows the variation of available Cd content in soil with organic fertilizer addition after 90 days of application of different types of organic fertilizers. It can be seen that for the same Cd pollution level of soil, with the increase of organic fertilizer dosage, the changing trend of available Cd content in soil is similar, but the changing trend of available Cd content in soil with different Cd pollution levels is different.

In mild Cd-contaminated soil (**Figure 2A**), the available Cd content decreased only when the organic fertilizer

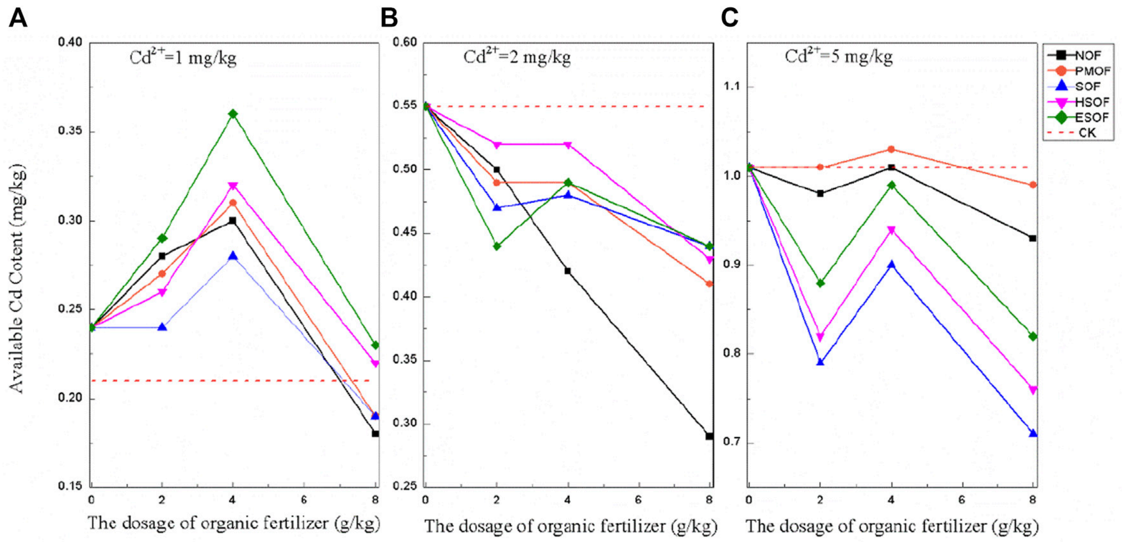

FIGURE 2 | Effects of organic fertilizer dosage on the contents of available Cd in soils with different Cd loads (**(A)**: Cd^{2+} = 1 mg/kg; **(B)**: Cd^{2+} = 2 mg/kg; **(C)**: Cd^{2+} = 5 mg/kg).

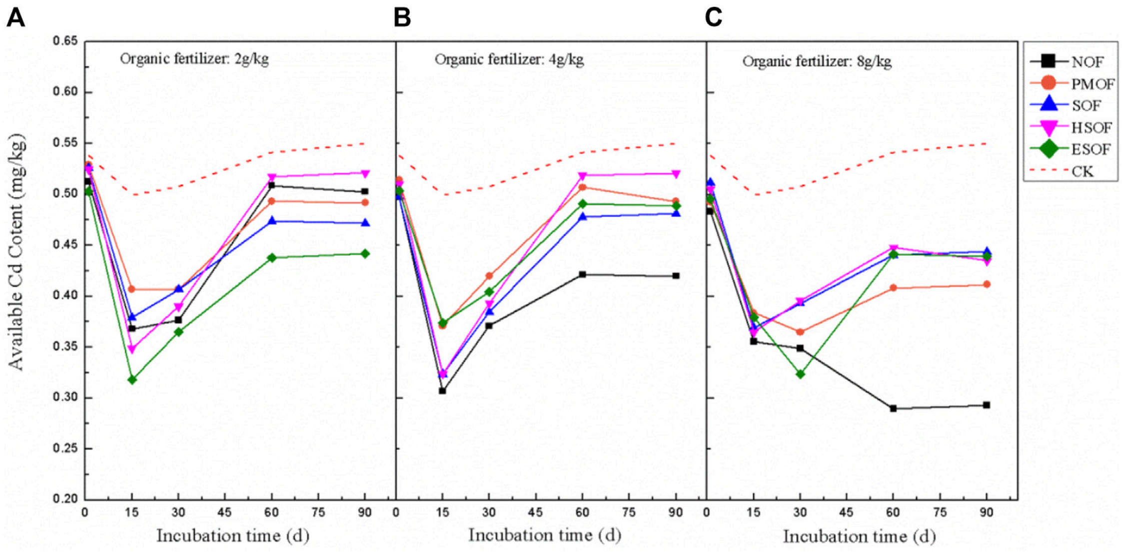

FIGURE 3 | Changes in available Cd content in soil treated with different dosages of organic fertilizers over time (**(A)**: OF = 2 g/kg; **(B)**: OF = 4 g/kg; **(C)**: OF = 8 g/kg).

addition increased to 8 g/kg, and was lower than the control level. SOF had the best effect on reducing the available Cd content, which was reduced by 20.83% compared with the control. In moderate Cd-contaminated soil, it can be found from **Figure 2B** that all kinds of organic fertilizers could significantly reduce the soil's available Cd content, and there was a significant negative correlation between available Cd content and organic fertilizer dosage. Among them, the effect of NM was the most obvious. When the addition amount was 8 g/kg, the soil available Cd content decreased by 47.27% compared with the control (0.55 mg/kg). In the severe Cd-contaminated soil (**Figure 2C**), the soil available Cd content increased first and then decreased with the increase of organic fertilizer addition. Except that PM was useless at medium and low dosages, other organic fertilizers had inhibitory effects on soil Cd availability, especially at the highest dosage (8 g/kg). The inhibitory order of various organic fertilizers on the soil's available Cd content was SOF > HSOF > ESOF > NOF > PMOF, and SM could reduce soil available Cd content by 29.70%.

TABLE 3 | Analysis of the relationship between bioavailable Cd and Cd chemical speciation.

Types of Organic fertilizer	Exe-Cd	Carb-Cd	FeMnOx-Cd	OM-Cd	Res-Cd
NOF	0.413^{a}	0.125	0.156^{b}	0.151	-0.728^{a}
PMOF	0.107^{a}	0.058	0.088^{b}	0.031	-0.528^{a}
SOF	0.339^{a}	0.211	0.171^{b}	0.167	-0.447^{a}
HSOF	0.201^{a}	0.039	0.282^{b}	0.071	-0.409^{a}
ESOF	0.441^{a}	0.142	0.115^{b}	0.084	-0.702^{a}

[a] Means a significant correlation at the 0.01 level (two-sided).
[b] Means a significant correlation at the 0.05 level (two-sided).

3.1.3 Effect of Organic Fertilizer on the Dynamic Change of Soil Available Cd Content

Taking moderate Cd-contaminated soil as an example, it can be observed from **Figure 3** that after the addition of five organic fertilizers, the content of available Cd in soil decreased first and then increased with the increase of incubation time, i.e., it reached the minimum at 15–30 days, then began to rise, and finally stabilized after 60 days. The available Cd are all lower than the control, which indicates that all kinds of organic fertilizers had inhibitory effects on available Cd in the soil at different times. When the addition amount of organic fertilizer was 2 g/kg, the soil available Cd content under the action of NOF, PMOF, SOF, HSOF, and ESOF decreased by 8.60%, 11.07%, 15.18%, 6.13%, and 19.30%, respectively, and ESOF had the strongest inhibitory effect on available Cd. When the addition of organic fertilizer was 4 and 8 g/kg, the soil available Cd content decreased by 24.24%, 11.07%, 12.71%, 5.30%, 11.07%, and 48.12%, 25.89%, 19.30%, 20.95%, 20.13% under the action of five organic fertilizers, respectively. NOF had the strongest inhibitory effect on available Cd.

3.2 Effects of Organic Fertilizer on Speciation of Cd in Soil

After 90 days of organic fertilizer application, the transformation of different speciation of Cd in soil tends to be balanced. The correlation analysis between available Cd and Cd speciation is shown in **Table 3**. It can be seen that the soil available Cd has a very significant positive correlation with soil Exe-Cd and Res-Cd, respectively, and a significant positive correlation with FeMnOx-Cd, indicating that the soil available Cd is mainly affected by the content of Exe-Cd, FeMnOx-Cd, and Res-Cd.

To order further determine the quantitative contribution of different speciation of Cd to soil available Cd, the optimal regression equation between soil available Cd and soil Cd speciation under different types of organic fertilizer was obtained by multiple regression analysis (**Table 4**). Exe-Cd and FeMnOx-Cd in soil have a significant positive contribution to available Cd, while Res-Cd has a significant negative correlation to soil available Cd, which indicated that the decrease of soil available Cd content was related to the decrease of soil Exe-Cd and FeMnOx-Cd content and the increase of Res-Cd content.

3.3 The Effect of Organic Fertilizer on the Cd Speciation Distribution in Soils With Different Levels of Cd Pollution

Figure 4 shows the average distribution of Cd speciation in Cd-contaminated soil with different degrees after different organic fertilizer treatments. It can be seen from the figure that the difference in the effect of organic fertilizer on the distribution of Cd speciation in different degrees of Cd contaminated soil is mainly reflected in Exe-Cd, FeMnOx-Cd, and Res-Cd, which is consistent with the correlation analysis in the previous section.

In mild Cd-contaminated soil, various organic fertilizers promoted the transformation of Cd to Exe-Cd. Compared with the control (24.87%), the content of Exe-Cd increased by 6.17%–20.28%, and the increase in HSOF treatment was the largest. The content of FeMnOx-Cd also increased by 2.90%–17.87%, and the increase in the SOF treatment group was the largest. However, the Res-Cd content decreased by 3.19%–14.38%, with the largest decrease in PMOF treatment. In moderate Cd-contaminated soil, the application of organic fertilizer decreased the contents of Exe-Cd and FeMnOx-Cd, while the Res-Cd content increased significantly. Exe-Cd and FeMnOx-Cd were reduced by 7.12%–28.50% and 0.07%–19.47%, respectively. Res-Cd increased by 19.74%–65.81%, and the ESOF treatment group had the largest decrease and increase. In severe Cd-contaminated soil, the content of Exe-Cd decreased significantly after adding organic fertilizer, while the contents of FeMnOx-Cd and Res-Cd increased slightly. Among them, Exe-Cd decreased by 7.25%–35.54%, ESOF decreased the most; the contents of FeMnOx-Cd and Res-Cd increased by 0.41%–42.41%, and 10.28%–34.79%, respectively, and ESOF and HMOF showed the largest increase in these two forms, respectively.

TABLE 4 | Multiple regression analysis of available Cd and Cd speciation.

Types of Organic fertilizer	Regression equation	R	R^2
NOF	$y = 0.067 + 2.084x_1 + 1.471x_3-2.762x_5$	0.819	0.671
PMOF	$y = 0.083 + 1.262x_1 + 1.253x_3-2.521x_5$	0.882	0.777
SOF	$y = 0.064 + 2.031x_1 + 1.592x_3-1.767x_5$	0.798	0.636
HSOF	$y = 0.059 + 1.801x_1 + 1.667x_3-1.581x_5$	0.846	0.716
ESOF	$y = 0.091 + 2.177x_1 + 1.133x_3-2.715x_5$	0.843	0.711

y Represents available Cd, x_1 represents soil Exe-Cd, x_3 represents soil FeMnOx-Cd, x_5 represents soil Res-Cd (mg/kg).

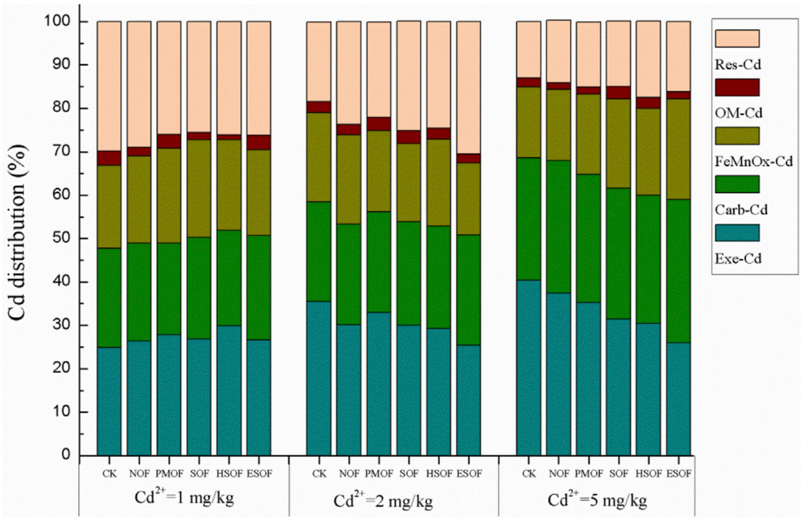

FIGURE 4 | Cd distribution among soil fractions after incubation with organic fertilizer from NOF, PMOF, SOF, HSOF, and ESOF at different dosages of application.

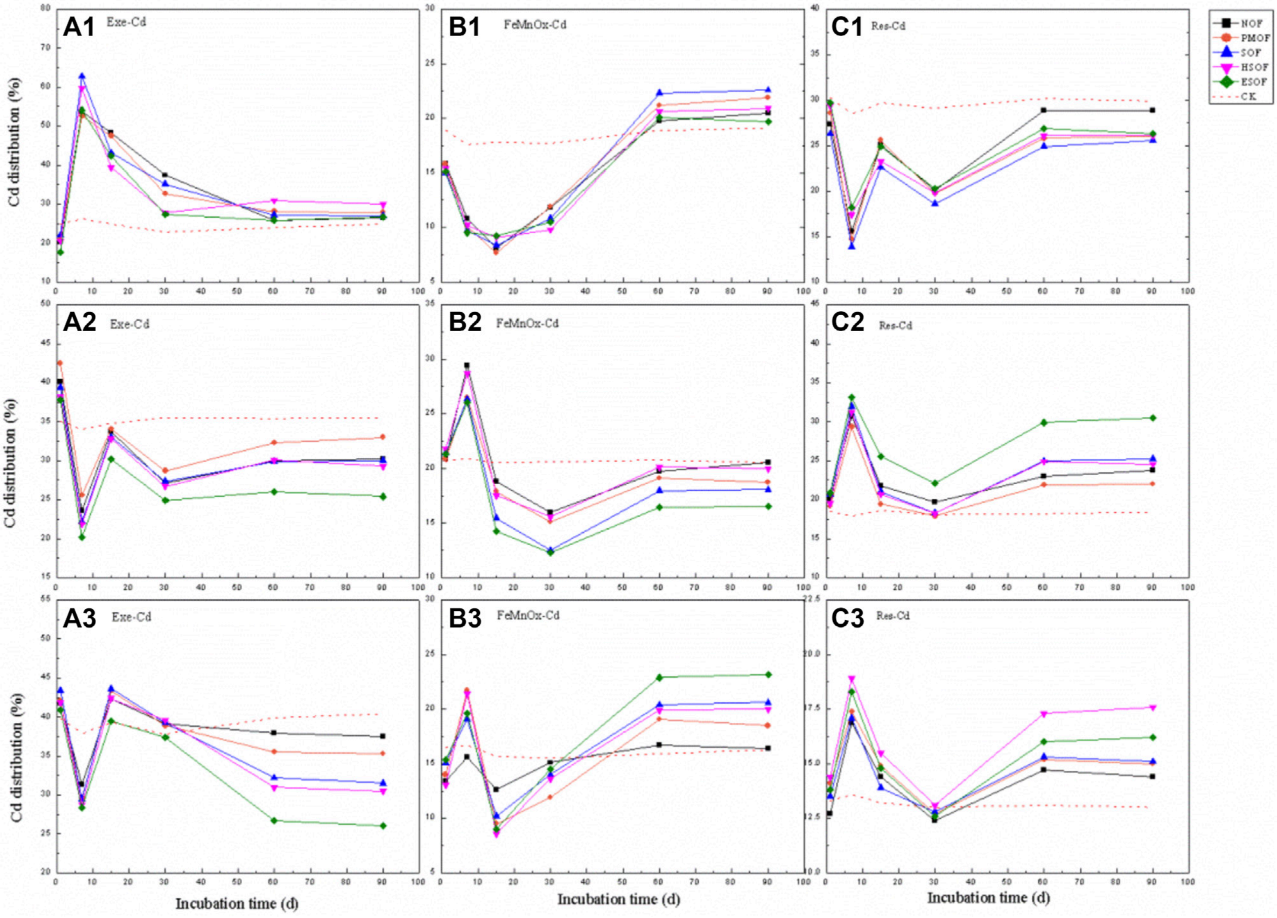

FIGURE 5 | Cd distribution among soil fractions after incubation with organic fertilizer from NOF, PMOF, SOF, HSOF, and ESOF for different incubation times.

3.4 The Effect of Organic Fertilizer on the Dynamic Change of Cd Speciation in Soil

The dynamic changes in the average distribution of three speciations of Cd in soils with different Cd pollution levels treated by organic fertilizer are shown in **Figure 5**. It can be seen that organic fertilizer does affect the speciation of Cd in soil, but the main influence is the distribution of Cd between different speciation. The changing trend of the same form of Cd is the same and the speciation of Cd reached a stable state at 60 days.

In mild Cd-contaminated soil, the content of Exe-Cd increased sharply at the initial stage of incubation and reached the peak at 7 days, then continued to decline and stabilized after 60 days, which was finally higher than the control. The contents of FeMnOx-Cd and Res-Cd decreased first and then increased on the whole, but the content of FeMnOx-Cd increased compared with the control, while the content of Res-Cd decreased. In the medium Cd-contaminated soil, the change of Exe-Cd content showed the opposite trend to that in low-concentration Cd soil before 30 days of incubation, which decreased sharply at the beginning of incubation, then fluctuated and increased and stabilized after 60 days, and was finally higher than the control. FeMnOx-Cd and Res-Cd reached the highest values at 7 days and then reached stability after 60 days. Finally, the content of FeMnOx-Cd decreased compared with the control, while the content of Res-Cd increased. In severe Cd-contaminated soil, the variation trend of each form was similar to that in moderate Cd-contaminated soil. Among them, the decrease and increase of Exe-Cd and FeMnOx-Cd contents in ESOF were the largest, respectively. but the increase of Res-Cd in HSOF was the largest.

4 DISCUSSION

Purple soil is weathered from purple sedimentary rocks and is concentrated in hilly areas of Sichuan and Chongqing. According to its pH and calcium carbonate content, purple soil can be divided into three subgroups: acidic, neutral, and calcareous purple soil (Yang, 2004). The test soil in this experiment was collected from Chongqing, belonging to calcareous purple soil. The heavy metal content of farmland soil in Chongqing was deeply affected by geochemical characteristics such as soil parent material and was also strongly affected by human factors such as industry, mining, and modern agriculture. Among them, Cd was the heavy metal with the highest proportion of exceeding the standard and the highest accumulation level in the region (He, 2004; Jia et al., 2018). The Southwest region where Chongqing is located in a variety of cropping systems with rice and maize, and its grain yield also accounts for a considerable proportion of the country. Purple soil is one of the main agricultural soils in Southern China, and Sichuan Basin is the most concentrated, accounting for more than 70% of the area (Yang et al., 1992). Therefore, heavy metal pollution in farmland, especially Cd pollution, will seriously endanger human health. The application of bio-organic fertilizer can not only change the physical and chemical properties of soil, and improve soil fertility, but also improve the living environment of soil microorganisms, increase soil enzyme activity, and improve the heavy metal pollution of soil, which is crucial to the sustainable development of local agriculture (Yu and Zhao, 2013).

4.1 The Change of Cd Speciation in Soil

The morphological characteristics of heavy metals in soil are important indicators to reveal the migration and transformation of heavy metals and bioavailability (Liu et al., 2020). Related studies have also shown that heavy metals in soil combine with different carriers into various forms, and different forms of heavy metals reflect different bioavailability (Huang et al., 2014; Liu et al., 2014; Kumar et al., 2021), which is further reflected in the change of soil available Cd content. According to the five-stage grouping method proposed by Tessier et al. (1979), heavy metals can be divided into exchangeable, carbonate-bound, Fe-Mn oxidized, organic-bound and residual states. Among them, the exchangeable and carbonate-bound heavy metals are easy to dissolve in the environment, and the exchangeable heavy metals are the most susceptible to biological utilization, with the strongest toxicity. Fe-Mn oxidized heavy metals can also be released when the redox potential changes, which is potentially effective for organisms. Residue heavy metals combined with sediments most firmly will not be absorbed, so their activity is minimal. The results of this study showed that organic fertilizer mainly affected the contents of Exe-Cd, FeMnOx-Cd, and Res-Cd in soil, but had little effect on the contents of Carb-Cd and OM-Cd, and the effect was related to Cd content in the soil. Liu et al. (2020) found that bio-organic fertilizer increased the pH value of paddy soil, promoted the transformation of acid-soluble Cd to oxidizable Cd, and reduced the bioavailability of Cd in soil. In this paper, the pH value of organic fertilizer was 8.06–8.12, and the pH value of gray-purple soil was 8.15, which were all weakly alkaline. The effect of organic fertilizer on soil pH value was minimal, so the addition of organic fertilizer almost did not affect the content of Carb-Cd. In heavy Cd-contaminated soil, organic fertilizer reduced the contents of Exe-Cd and FeMnOx-Cd and increased the content of Res-Cd, which was similar to many research results. Xie et al. (2018) showed that with the increase in humic acid application rate, the exchangeable Cd content in soil decreased significantly. The residual Cd content increased by 53.6%–113.9%. However, when humic acid was added, the pH value of the soil did not change significantly. The reason for the decrease of available Cd may be that humic acid could have a series of adsorption, complexation, and chelating effects with Cd^{2+}. The combination of its products with soil clay particles strengthened the adsorption ability of soil clay particles to Cd^{2+}. At the same time, humic acid itself was adsorbed on the surface of soil colloid as an adsorbent, which increased the adsorption point of soil particles and further promoted the transformation of exchangeable Cd^{2+} to a stable state. Liu et al. (2014) found that the application of bioorganic fertilizer could promote the transformation of acid-soluble Cd to reducible Cd by increasing soil organic matter content, CEC, and pH, and showed that different organic fertilizers could reduce the content of available Cd in soil by increasing the content of soil organic matter. The mechanism was that organic fertilizer could directly increase the content of soil organic matter, and its various functional groups (-COOH, -OH, -CO, etc.,) and organic matter with a large specific surface area could form insoluble metal-organic complexes with heavy metals to enhance the adsorption of heavy metals (Zhou et al., 2018). Soil organic matter also has reducibility, Fe-Mn oxides of heavy metals can be released under reduction conditions, resulting in FeMnOx-Cd content increased. Moreover, organic matter can also improve soil structure, thereby indirectly changing the speciation distribution of Cd in soil. In addition, some studies have found that the change of soil microbial biomass and enzyme activity under organic fertilizer application is one of the important effective ways to affect the occurrence of Cd in soil (Huang et al., 2017). Xu et al. (2015) found that heavy metals significantly affected MBC, MBN, and various enzyme activities in soil. At the same time, the activities of UA, ACP, and DH in soil were significantly correlated with the absorption of heavy metals by rice. Zhang et al. (2020) showed that the application of organic fertilizer to reduce the content of soil acid extractable Cd was mainly achieved by increasing the content of soil organic matter, soil dehydrogenase activity, and microbial biomass carbon content. Therefore, it is suggested that in future studies, the influence mechanism of microbial biomass and enzyme activity in organic fertilizer on Cd forms in soil should be studied in depth. In this study, the ability of different types of organic fertilizers is different but does not change the evolution of specific speciation of Cd, which may be due to the morphological differentiation mechanism of various organic fertilizers on heavy metals in soil being similar.

4.2 The Passivation Effect of Cd in Soil

The results showed that the passivation effect of soil Cd increased with the increase of organic fertilizer application rate, and in different Cd pollution levels of soil, the passivation effect of high organic fertilizer application amount (8 g/kg) in moderate Cd pollution soil was the best, while the passivation effect of medium organic fertilizer application amount (2 g/kg) in mild Cd pollution soil was the worst. Lu (2003) studied the effect of bio-organic fertilizer on the bioavailability of Cd in soil. It was found that the higher the Cd content in the soil, the more obvious the passivation effect of bio-organic fertilizer, which was similar to the results of this experiment. However, Liu et al. (2009) studied the effects of different types of organic fertilizers and application rates on soil Hg pollution, migration, and accumulation. The results showed that organic fertilizer had the best effect on low-level Hg-contaminated soil, which was contrary to the results of this experiment. Thus, although the effect of bio-organic fertilizer on the remediation of heavy metals in soil was studied, the results were different due to the different types of organic fertilizer, different treatment methods and experimental conditions, and different research objects. For the five organic fertilizers used in this experiment, their Cd content was 0.18–0.31 mg/kg, while the content of mild Cd contaminated soil was set to 1 mg/kg. The addition of organic fertilizer increased the Cd content in mild Cd contaminated soil by 18%–31%, which also greatly affected the final passivation effect of organic fertilizer. Organic fertilizer is rich in humus. Studies have shown that the chelation and adsorption of humus on metal ions coexist. When the concentration of metal ions is high, the exchange adsorption is dominant, and when the concentration is low, the chelation is dominant. The influence of the chelation on the migration of metal ions depends on whether the formed chelate is insoluble or soluble. When humus and metal ions form soluble chelate, it promotes the migration of heavy metals, and if insoluble chelate is formed, it hinders the migration of heavy metals. The chelate formed by humic acid and metal ions in humus composition is generally insoluble and can reduce the activity of heavy metals (Sahu and Banerjee, 1990; Swift et al., 1995), and the chelate formed by fulvic acid and heavy metal ions is soluble, thus promoting the mobility of heavy metal ions in the soil. In this study, the passivation effect of high organic fertilizer application amount in heavily polluted soil was the best, and the passivation effect of medium and low biological organic fertilizer application amount in low polluted soil was the worst. The reason may be that when the Cd content in soil was high, various functional groups contained in organic fertilizer and organic matter with a large specific surface area could form an insoluble metal-organic complex by complexing with heavy metals, and the passivation effect was the best. When the Cd content was low, the Cd contained in organic fertilizer and the chelate formed by fulvic acid and Cd improved the availability of Cd in soil, resulting in the worst passivation effect.

5 PRACTICAL IMPLICATIONS OF THIS STUDY

Heavy metal pollution, as a more serious type of soil pollution, has become increasingly serious, threatening almost every country, especially cadmium, which is particularly harmful to food safety and human health. Soil cadmium pollution control has become a difficult and hot spot in international research. Therefore, how to control cadmium pollution, and reduce the impact of polluted soil on the quality and safety of agricultural products, thereby reducing its harm to human beings, and achieving sustainable development of agriculture, is an important issue related to public's health. China is rich in organic fertilizer resources. It is convenient and economical to obtain materials, which not only play an important role in improving soil heavy metal pollution but also have great significance in improving land productivity. This is also incomparable to other inorganic improvement materials for controlling heavy metal pollution. Therefore, organic materials have broad application prospects and important significance in soil improvement. Future research is expected to study and launch organic fertilizer passivation formulas suitable for different soil types and different heavy metal pollution.

6 CONCLUSION

This paper studied the regulation of different organic fertilizers on different degrees of Cd-contaminated soil and provided theoretical support for the remediation of Cd-contaminated gray-purple soil in Southwest China. The specific conclusions are as follows:

The effects of various organic fertilizers on Cd availability in purple soil are closely related to soil pollution and organic fertilizer dosage. In mild Cd contaminated soil, a low dosage (<4 g/kg) of organic fertilizer promoted the activation of Cd, and only showed an inhibitory effect when the dosage increased to 8 g/kg. In moderately Cd-contaminated soil, each organic fertilizer significantly inhibited the availability of soil Cd, and the inhibition effect increased with the increase of organic fertilizer dosage. In the severe Cd-contaminated soil, except that PMOF had no inhibitory effect on soil Cd availability at medium dosage, other organic fertilizers showed certain inhibitory effects at different application rates, and the effect was significant at low and high dosages. Therefore, it is highly recommended to use the five types of organic fertilizers mentioned in this paper to passivate moderately Cd contaminated soils.

The dynamic changes in soil available Cd content and morphological transformation were consistent after adding organic fertilizer, and both of them stabilized after 60 days of organic fertilizer application. Therefore, more definitive results are generally monitored after 60 days in practical applications. The availability of soil Cd is mainly restricted by Exe-Cd, FeMnOx-Cd, and Res-Cd. Exe-Cd and FeMnOx-Cd have significant positive contributions to soil available Cd, and Res-Cd has significant negative contributions to soil available Cd.

The effect of organic fertilizer on Cd passivation in purple soil was significantly different in different polluted soils. In general, in moderate and severe Cd-contaminated soil, the effectiveness of organic fertilizers on soil Cd was significantly inhibited, among which NOF and SOF were the best, while in mild Cd-contaminated soil, the passivation effect of organic fertilizers on soil Cd was the worst, especially ESOF.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**supplementary material**, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

Conceptualization: LW and SL, Data curation: LW and JL ,Formal analysis: LW, Funding acquisition: LW and SL, Investigation: LW and SQL, Methodology: LW and SQL, Project administration: LW and SL ,Resources: LW and SL, Supervision: LW, Writing-original draft: LW ,Writing-review and editing: LW and JL.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvs.2022.895646/full#supplementary-material

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Conflict of Interest: LW, SL, and JL were employed by the company Shaanxi Provincial Land Engineering Construction Group Co,. Ltd. and SQL was employed by the Zhejiang Dongda Environment Engineering Co,. Ltd.