Research Article

Aging Process of Cadmium, Copper, and Lead under Different Temperatures and Water Contents in Two Typical Soils of China

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Aging process of exogenous heavy metals in soil is significant for reducing their environmental risk due to the redistribution of species of soil heavy metals. A red soil (ultisol) and a brown soil (alfisol) were selected to investigate the aging process of cadmium (Cd), copper (Cu), and lead (Pb) under different regimes of temperature and water content. Most introduced heavy metals were all transformed from dissolved fraction to more stable fractions within 5 days of incubation. During incubation, most Pb existed in the fraction bound to Fe/Mn oxides, while exchangeable and carbonate-associated fraction was the dominant portion for Cd and Cu, suggesting that the transformation rate followed the order: Pb > Cu > Cd. The exchangeable and carbonate-associated fraction in red soil, which was characterized with higher pH and Fe/Al/Mn oxides and lower organic matter (OM), was significantly higher than that in brown soil, implying that soil OM was the important factor affecting the aging process of soil heavy metals in the present study. In addition, increases of temperature and soil water content can accelerate the transformation of most introduced Cd, Cu, and Pb to more stable forms in the soils. The results indicated that soil properties, environmental factors (i.e., temperature and water content), types of heavy metals, and pollution time can significantly affect the aging process of exogenous heavy metals.

1. Introduction

Soil pollution by heavy metals has led to great concerns in the past few decades [1–3]. Heavy metals in soil can be absorbed by crops and accumulated in foods, eventually generating adverse impact on plant growth and threatening human health through the food chain [4–8]. In addition, excess heavy metals in surface soil can migrate downward easily to pollute groundwater inducing high health risk [9, 10]. Excess heavy metals in soil are often derived from anthropogenic activities, such as mining, fertilization, traffic, and industry [2, 11–15]. For example,

in acid mine drainage, concentrations of heavy metals can be up to tens of mg per liter, even hundreds of mg per liter [16], which often leads to severe heavy metal pollution of soils surrounding mines.

When these exogenous heavy metals, especially soluble form, were discharged into the soil, they can be fixed via incorporation into crystal lattices, diffusion into micropores, or formation of metal precipitates on the surfaces of soil minerals [17] and present relatively low bioavailability and mobility. This progress terms the aging of heavy metals and is crucial for reducing the environmental risk of soil heavy metals [18]. The aging process of soil heavy metals is time dependent [19]. The

short-term aging process is predominantly controlled by solid-liquid distribution (mainly adsorption). Previously research reported that rapid reduction of bioavailable heavy metals often occurred within 10–20 days after adding heavy metals [20–22]. After that, heavy metals adsorbed on the surface of soil are further slowly fixed by micropore diffusion, cavity entrapment, occlusion in solid phases by coprecipitation, surface precipitation, and so on [23, 24]. The two steps of the aging process are both affected significantly by types of heavy metals, soil properties, and circumstance conditions. It was reported that Cd shows a lower tendency to be fixed into unavailable forms than Zn or Cu [25]. Soil organic matter (OM), clay and Fe/Al oxides, meanwhile, are significant for aging of soil heavy metals [26, 27]. It was reported that Cu trends to bind onto OM in some size fractions of soil particles [28]. Al oxides play a more crucial role than Fe oxides in controlling the rate of arsenic (As) aging [29]. Aging process can be accelerated or retarded obviously under different circumstance conditions as well. High temperature generally increases and accelerates the diffusion of heavy metal ions in micropores and form inner surface, further accelerating the transformation of soil heavy metals [23, 30]. Zheng et al. reported that waterlogging of soil facilitate the transformation of heavy metals from bioavailable fraction to a more stable fraction by changing soil pH, Eh, and hydrous oxide content [20]. Higher salinity also can retard the stabilization of heavy metals during aging [31].

Though the aging of soil heavy metals has been studied extensively under various circumstance conditions, some inconsistent results of the aging process of soil heavy metals have been reported. Liang et al. reported that only 1.1–8.1% decreased in Pb bioaccessibility during 76 weeks [32]. However, Jalali and Khanlari obtained that average 79% heavy metals (Cd, Cu, Pb, and Zn) become nonexchangeable fraction after 28 days of incubation [33]. It was also found that the percent of exchangeable fractions of heavy metals (Cd, Cu, and Pb) to nonexchangeable fraction decreased by 32.39%–74.11% after 35 days of incubation [20]. Thus, it is meaningful to further explore the aging process of soil heavy metals. In addition, the pH value of red soil is generally lower than brown soil, and the content of metal oxides of red soil is generally higher than brown soil. However, alkaline red soil located in limestone area is typical in southern China and some acid brown soil also can be found in northern China. In the present study, an alkaline red soil (ultisol) containing higher metal oxides and an acidic brown soil (alfisol) containing lower metal oxides, which was not consistent with soil properties in most other studies, were used to study the aging process of heavy metals under different regimes of temperature and water content. This study can provide more information for aging mechanisms of soil heavy metals which contributes to assessing environmental risk of soil heavy metal pollution.

2. Material and Methods

2.1. Soil Sampling and Characterization. Red and brown surface soils (0–20 cm) were sandy loam ultisol and loamy sand alfisol and were collected from a hilly forest in Fujian Province and farmland in Shandong Province, respectively, in China. The soil samples were air-dried, sieved through a 2 mm polyethylene sieve, and then stored in polyethylene Ziploc bags before further analysis and soil incubation. Soil pH was measured with a pH meter (Mettler Toledo FE20, Switzerland) at a soil to water ratio of 1 : 2.5. Soil texture was analyzed using a laser particle size analyzer (Microtrac S3500, USA). Soil OM was measured by the $K_2Cr_2O_7$ oxidation method [34]. Free crystalline and amorphous oxides Al, Fe, and Mn (DCB-Al, DCB-Fe, and DCB-Mn) were extracted by dithionite-citrate-bicarbonate (DCB) extraction [34]. Cation exchange capacity (CEC) was determined by the $BaCl_2$ compulsive exchange method [35]. Subsamples of soils (0.2 g) were digested with 3 mL HNO_3, 1 mL $HClO_4$, and 1 mL HF in closed Teflon vessels for 5 h at 165°C. After cooling, the vessels were transferred to an electric hot plate (160°C) to eliminate silicon and any remaining HF. After the white smoke disappeared, the samples were taken off, and 1 mL HNO_3 was added, and then were adjusted to 10 mL with ultrapure water to measure heavy metals by inductively coupled plasma-optical emission spectrometry (ICP-OES) (SPECTRO ARCOS EOP, SPECTRO Analytical Instruments GmbH, Germany) [2]. To ensure analytical quality, geochemical standard soils (GSS-1 and GSS-2), provided by the National Research Center for Geoanalysis of China, were used to validate the analytical method. The recoveries of the standard samples ranged from 90% to 110%.

2.2. Soil Incubation. 50 g of the soil sample was weighed into a 100 mL plastic beaker. A 5 mL of the mixed stocked solution of Cu $(NO_3)_2$ (Cu: 2 g/L), Pb $(NO_3)_2$ (Pb: 2 g/L), and Cd $(NO_3)_2$ (Cd: 30 mg/L) was added to the soil. The amounts of metals spiked were 200 mg/kg for Cu and Pb and 3 mg/kg for Cd, respectively, which were higher than the risk screening values for soil contamination of the agricultural land of China (GB 15618-2018) [36]. Certain water content of the incubation soils was adjusted by adding deionized water. All samples were mixed thoroughly and then covered with a piece of parafilm with some pores to allow air influx and avoid the evaporation of soil water. For the experiment of temperature effect, all soil samples were stored in the dark at 5, 10°C, and 25°C; the deionized water was added to maintain the soil water content of 20% every 2 days. For the experiment of water content effect, all soil samples were subjected to four water content conditions (i.e., 10%, 20%, 30%, and waterlogging (a 1 cm layer of water over the soil samples)) and stored in the dark at 25°C. Soils were sampled at different aging periods (5, 15, 45, 85, and 145 days) after adding heavy metals, then analyzed for their geochemical fractions. All treatments were conducted in triplicate.

2.3. Geochemical Fraction Analysis of Heavy Metals. The sequential extraction of heavy metals in soils was carried out following the modified European Community Bureau of Reference (BCR) sequential extraction procedure [37]. This procedure separates the heavy metals in soils into three fractions, i.e., exchangeable and carbonate-associated (F1), reducible (bound to Fe/Mn oxides, F2), and oxidizable (bound to OM, F3) fractions, which are extracted by 0.11 mol/L acetic acid solution, 0.1 mol/L hydroxylamine

hydrochloride solution adjusted to pH 2.0 with HNO_3, and 1 mol/L ammonium acetate solution after digestion with H_2O_2, respectively. To obtain the mass balance of heavy metals in the soils, the residual fraction (F4) was measured after acid digestion using the procedure described above for total metal determination. The recoveries, which were defined as the sum of F1, F2, F3, and F4 divided by the total content, ranged from 108% to 120%.

2.4. Statistical Analysis. One way ANOVA test was used to statistically analyze the difference between the data sets. Pearson's correlation was performed to obtain the correlation of heavy metal speciation during aging experiments. Statistical analyses were performed with the statistical software package SPSS version 20.0 for Windows.

3. Results

3.1. Soil Characteristics and Geochemical Fractions of Heavy Metals in the Native Soils. The soil characteristics were shown in Table 1. The red soil was slightly alkaline (pH = 7.17) and brown soil was more acidic than red soil (pH = 4.58). Low soil pH is considered to have an adverse effect on the stabilization of exogenous heavy metals [38, 39]. Brown soil from farmland contained more OM, indicating a relatively high ability to bind and retain heavy metals [40]. DCB-Fe/Al/Mn oxides, including free crystalline and amorphous Fe/Al/Mn oxides, play a significant role in the aging of soil heavy metals [18]. Concentrations of DCB-Fe/Al/Mn in red soil were higher than that of brown soil. Fe/Al/Mn oxides in soils can strongly bond heavy metals via coprecipitation, adsorption, surface complex formation, ion exchange, and penetration of the crystal lattice [41]. The CEC values of the two soils were comparable with 5.41 and 5.89 $cmol_c$/kg, respectively. Sand was the major fraction for the red and brown soils, with values of 61.2% and 81.2%, respectively. The concentrations of Cd, Cu, and Pb were 0.09, 18.2, and 29.2 mg/kg in red soil and 0.09, 11.4, and 18.9 mg/kg in brown soil, respectively, and lower than risk screening values for soil contamination of agricultural land of China (GB 15618-2018) [36], indicating no pollution by Cd, Cu, and Pb.

As mentioned above, the soils were both not polluted by Cd, Cu, and Pb. F1 fraction proportion of Cd was 25.2% and 34.2% in red soil and brown soil, respectively (Figure 1). Due to low content, an F3 fraction of Cd cannot be detected for both soils. The bioavailable fraction of Cu (i.e., F1 fraction) was relatively low in red and brown soils, with values of 2.7% and 10.15%, respectively, and the proportion of F4 fraction was highest. For Pb, the percentage of F1 fraction was 26.4% in red soil, while the lower percentage of F1 fraction was found in brown soil (5.0%). Moreover, the F2 fraction of Pb was high in both soils. The total concentration of heavy metals and bioavailable fraction concentrations of heavy metals in native soil were both lower than spiked heavy metals; hence the effect of Cd, Cu, and Pb in native soil on the aging process can be ignored.

3.2. Heavy Metal Aging under Different Incubation Temperatures. The time-dependent fraction transformations of Cd, Cu, and Pb under different incubation temperatures were shown in Figures 2–4, respectively. The concentration of F1 fraction was extremely increased when exogenous heavy metals were added in the soils. Thus, the proportion of F1 fraction was predominant for Cd and Cu during all incubation experiments, and the proportion of F1 fraction of Pb was relatively high as well. The proportions of F1 fraction of Cd and Pb slightly reduced for 5–45 days of incubation for all cases and changed less after 45 days. For Cu, the proportion of F1 fraction changed less with incubation time at 5°C and 10°C, while the proportion of F1 fraction in the two soils both slightly decreased with incubation time at 25°C. After 145 days of incubation at a different temperature, the proportions of F1 fraction of Cd, Cu, and Pb ranged in 82.2%–90.0%, 51.0%–74.9%, and 27.2%–43.8%, respectively.

During the whole aging process under different temperatures, Pb in the F2 fraction was predominant, ranging from 46.1% to 55.5% in the red soil and 55.1% to 67.1% in the brown soil, respectively. A relatively lower proportion of F2 fraction of Cd and Cu was found during the incubation period, ranging from 6.8% to 18.5% for Cd and 15.1% to 33.3% for Cu, respectively. The proportion of F2 fractions of Cd, Cu, and Pb changed less or slightly increased during 5–145 days of incubation for all cases, while the amount of F2 fraction of heavy metals was higher than that in native soils. F3 fractions of Cd, Cu, and Pb were all relatively low and gradually increased with incubation time. After incubation, percentages of F3 fraction ranged in 0.8%–4.8% for Cd, 2.4%–6.1% for Cu, and 2.4%–4.6% for Pb, respectively.

3.3. Heavy Metal Aging under Different Soil Water Contents. Change patterns of heavy metal geochemical fractions under different water content were shown in the Figures 5–7. The rapid decrease of F1 fraction of heavy metals was not observed, and F1 proportion of heavy metals was relatively high, which were consistent with the results of the experiments under different incubation temperatures. During the incubation period, the proportions of F1 fraction of Cd and Cu were slightly decreased. The proportion of F1 fraction of Pb slightly decreased first, then slightly increased after 45 days of incubation. After 145 days of incubation, the percentage of F1 fraction ranged from 77.3% to 87.3% for Cd, 46.1%–66.4% for Cu, and 24.8%–41.4% for Pb, respectively. F2 and F3 fractions of Cd slightly increased with incubation time. For Cu and Pb, the obvious change of F2 fraction with incubation time was not found, while the obvious increase of F3 fraction of Cu and Pb can be found with incubation time. The proportion of F4 fraction of Cd and Cu slightly increased with incubation time, but the F4 fraction was below 3.0% for Cd and 15.0% for Cu, respectively. For Pb, the low and unchanged proportion of F4 fraction was found, ranging from 5.6% to 7.0%.

TABLE 1: Physicochemical properties of the soil samples.

Soil samples	pH	CEC (cmol$_c$/kg)	OM (g/kg)	Soil texture (%)			Total heavy metal concentrations (mg/kg)			DCB-metal oxides (g/kg)		
				Clay	Silt	Sand	Cd	Cu	Pb	Al	Fe	Mn
Red soil	7.17	5.41	7.1	5.1	33.8	61.2	0.09	18.2	29.2	1.84	11.64	0.33
Brown soil	4.58	5.89	12.1	1.4	17.4	81.2	0.09	11.4	18.9	0.92	4.98	0.28
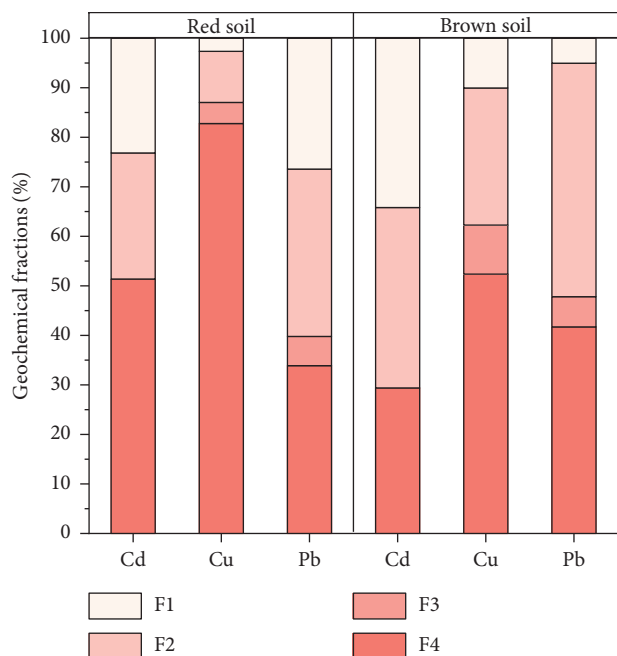
FIGURE 1: Geochemical fractions of heavy metals in native soil.

4. Discussion

4.1. Aging Process. In the present study, a rapid reduction of F1 fraction of Cd, Cu, and Pb was not observed, indicating that most spiked heavy metals (soluble form) had transformed into more stable fractions within 5 days of incubation in the tested soils. The result was not consistent with other studies, in which rapid reduction of bioavailable Cd, Cu, and Pb was found within 10–20 days after adding heavy metals [20–22]. The concentrations of heavy metals in other aging experiments were 30 mg/kg for Cd, 500 mg/kg for Cu and Pb, and higher than heavy metal concentrations in the present study, which might be the reason for the rapid reduction of bioavailable Cd, Cu, and Pb within 5 days. In addition, the difference in soil properties, such as OM, CEC, and Fe oxides, should be another reason for the rapid transformation of spiked heavy metals in the present study. Although the bioavailable fraction of spiked heavy metals was decreased in a short-time incubation, their concentration and proportion were still high, indicating a higher environmental risk.

The decrease of F1 fraction and the slight increase of other fractions during the incubation period indicated that F1 fractions transformed into more stable fractions after adding exogenous heavy metals. The results were also

supported by Pearson's correlation (Table 2). Under different incubation temperatures, the correlations between F1 and F2 fractions of Cd, Cu, and Pb were all negative and very significant ($p < 0.01$). Similarly, the very significant ($p < 0.01$) and negative correlations between F1 and F2 fractions were also observed for Cd, Cu, and Pb under different soil water content. The results indicated that most introduced heavy metals converted to F2 fraction during incubation. In addition, other fractions presented a strong correlation as well. For the aging experiment under different temperatures, some significant ($p < 0.05$) or very significant ($p < 0.01$) correlations among F2, F3, and F4 were observed. Significant ($p < 0.05$) or very significant ($p < 0.01$) correlations between F2 and F3 fractions of heavy metals were also found for the aging experiment under different soil water content. The result both indicated that the transformation among F2, F3, and F4 should occur during incubation.

4.2. Influence of Factors on Aging of Soil Heavy Metals. Soil property is a crucial factor affecting the aging process of heavy metals [23, 28, 42]. Fe/Mn oxides in soils can strongly bond heavy metals via coprecipitation, adsorption, surface complex formation, ion exchange, and penetration of the crystal lattice [40]. Higher soil pH can enhance the negative charge on the surface of soil particles and induce precipitation of heavy metals [43]. In addition, higher pH can promote precipitation/nucleation by the formation of Me (OH)$^+$ on the surfaces of soil solids, where proton dissociation from water molecules often takes place more readily than in bulk solutions [23]. The pH and content of DCB-Al/Fe/Mn were lower in brown soil than red soil, which seems to conclude the stronger ability of red soil to stabilizing exogenous heavy metals. However, it can be found that the obvious patterns of the speciation distribution of heavy metals were higher for the F1 and F3 fractions (ANOVA, $p < 0.05$) and lower for the F2 fraction (ANOVA, $p < 0.05$) in the red soil compared to the brown soil. Notably, the content of soil OM of brown soil was higher than red soil. Thus, it can be deduced that soil OM should be more important than other soil properties for heavy metal aging in the present study. Soil OM possesses a great number and variety of functional groups, which enhance the heavy metal adsorption capacity primarily by surface complexation, ion exchange, and surface precipitation [43–45]. Beyond that, the dominant fraction of different heavy metals was obviously different during the incubation period. It was observed that most Pb existed in F2 fraction, while dominant portions of Cd and Cu were F1 fraction during the whole incubation period. The result suggested that the transformation rate followed the order: Pb > Cu > Cd.
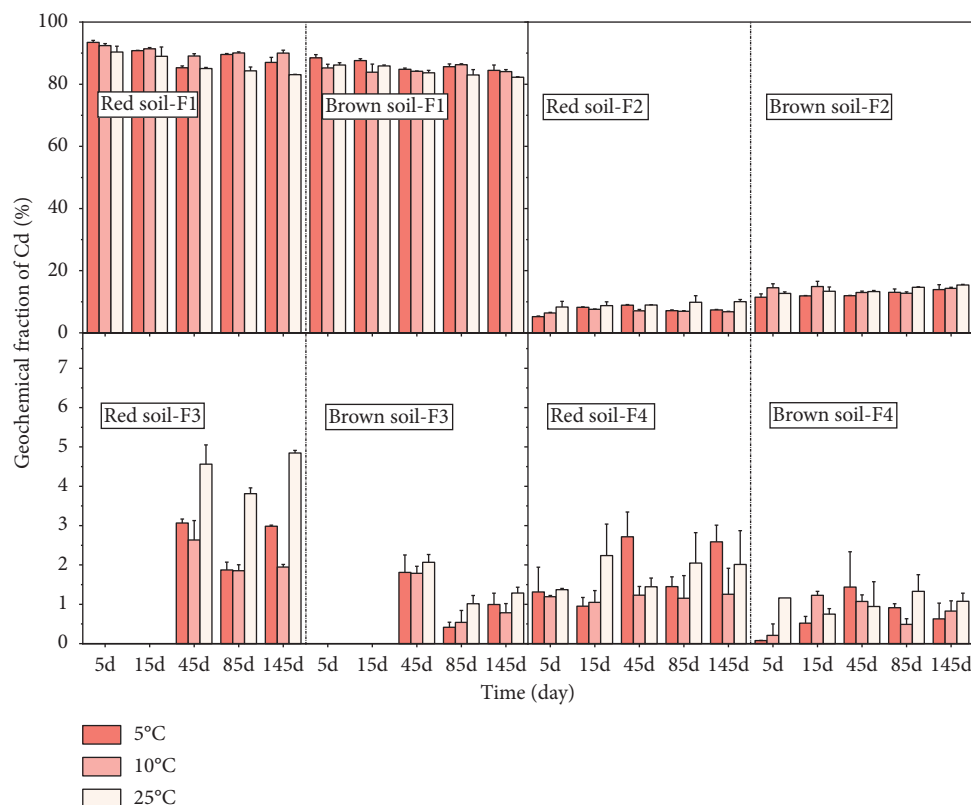
FIGURE 2: Changes in Cd fractions in soils at different temperatures as a function of contact time.

TABLE 2: Pearson's correlation of heavy metal speciation during aging experiments.

Heavy metal speciation		F1	F2	F3	F4
Cd	F1	1	−0.624**	−0.336*	−0.176
	F2	−0.0815**	1	−0.371*	−0.336*
	F3	−0.375*	−00.212	1	0.488**
	F4	−0.029	−0.443*	0.578**	1
Cu	F1	1	−0.950**	0.268	−0.810**
	F2	−0.971**	1	−0.526**	0.608**
	F3	0.116	−0.315	1	0.117
	F4	−0.870**	0.759**	0.036	1
Pb	F1	1	−0.991**	0.640**	−0.200
	F2	−0.993**	1	−0.695**	0.154
	F3	0.519**	−0.590**	1	−0.258
	F4	−0.293	0.251	−0.465**	1

*Correlation is significant at the level (2-tailed). **Correlation is significant at the 0.01 level (2-tailed); values in italics denote Pearson's correlation coefficient for aging experiments under different temperatures, $n = 30$; underlined values denote Pearson's correlation coefficient for aging experiments under different water contents of soils, $n = 40$.

F1 proportions of Cd and Cu at 5°C and 10°C were both significantly higher than that at 25°C during incubation (ANOVA, $p < 0.05$ for Cd and $p < 0.01$ for Cu). While F2 fractions of Cd at 5°C and 10°C were both significantly lower than that at 25°C (ANOVA, $p < 0.05$). For Cu, only brown soil presented higher F2 fraction at 5°C and 10°C than that at 25°C (ANOVA, $p < 0.05$). The significant difference for Pb was not found at different incubation temperatures (ANOVA, $p < 0.05$), but after incubation, F1 fraction of Pb at 25°C was lower than that at low temperature and F2 fraction of Pb at 25°C was higher than that

at low temperature. The results indicated that enhancing incubation temperature can accelerate the transformation of spiked heavy metals. It has been reported that increasing temperature can accelerate the adsorption of heavy metal ions on the soil particle surface and the diffusion of heavy metal ions into interlayers of soil minerals, affecting the aging mechanisms [23, 30]. The result agreed with the aging process of As at different temperatures [30].

During incubation, the difference of F1 fraction among various water content experiments did not reach a
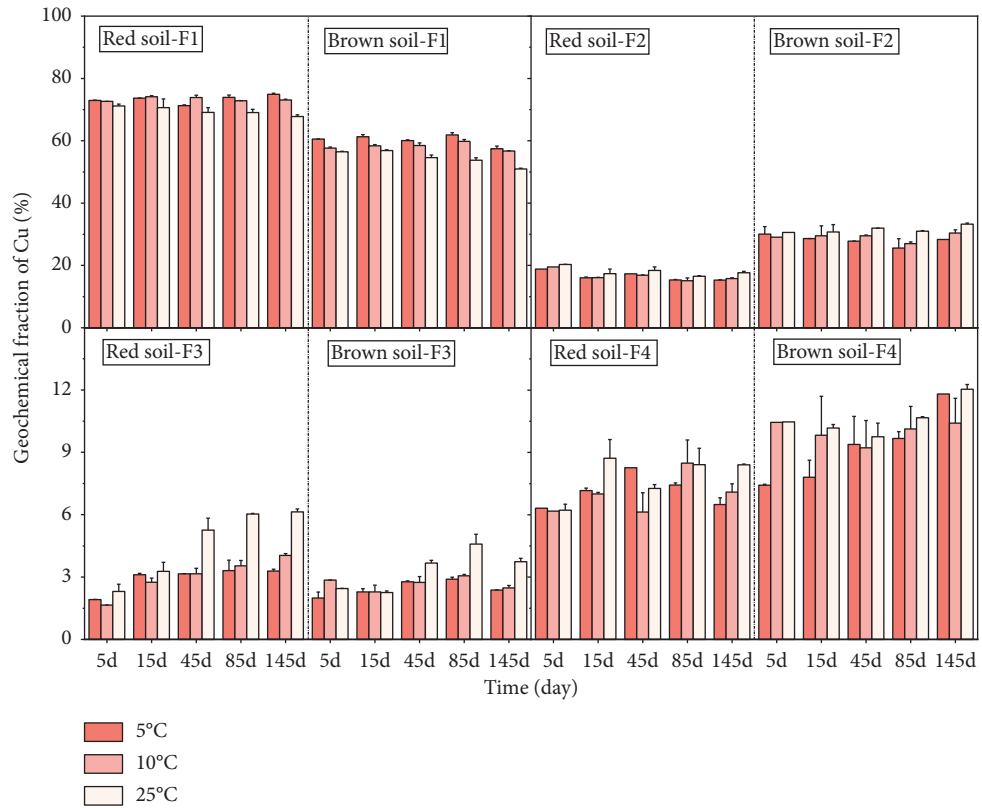
FIGURE 3: Changes of Cu fractions in soils at different temperatures as a function of contact time.
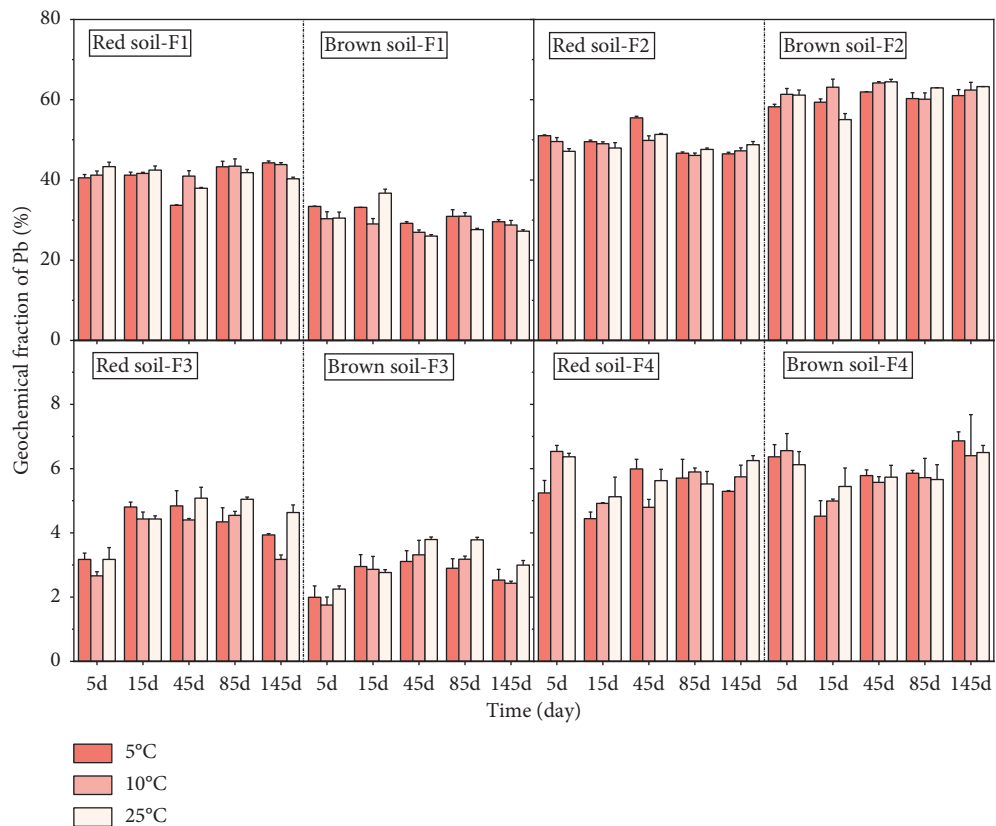

FIGURE 4: Changes of Pb fractions in soils at different temperatures as a function of contact time.
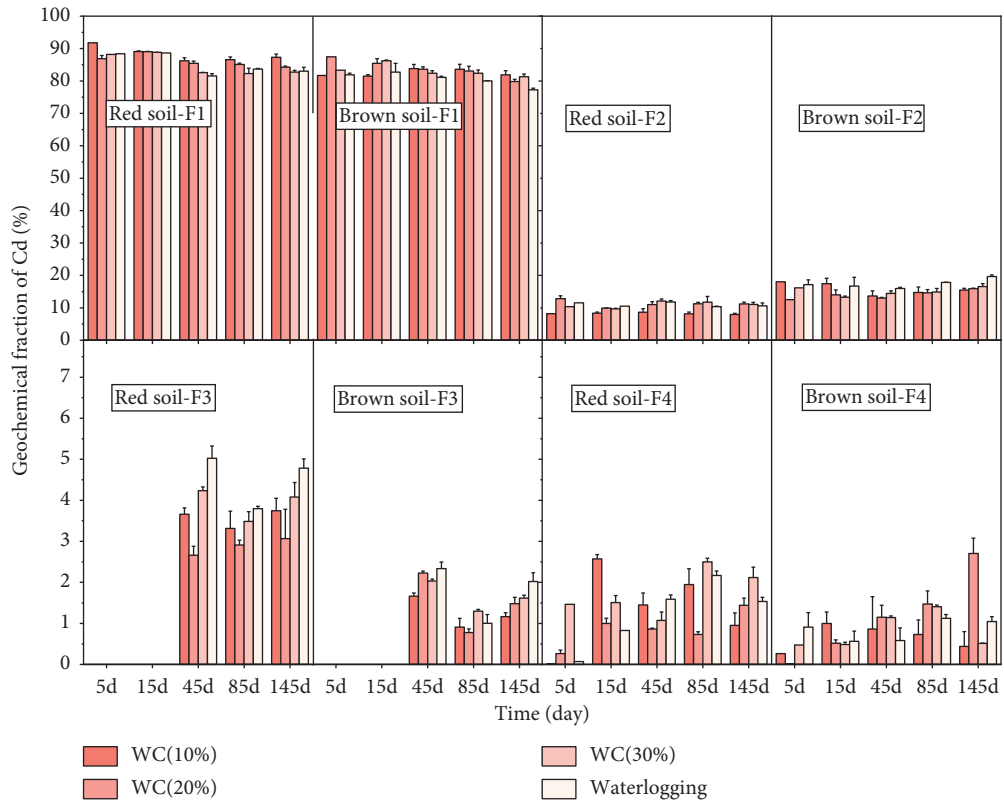
FIGURE 5: Changes of Cd fractions in different soil water contents as a function of contact time.
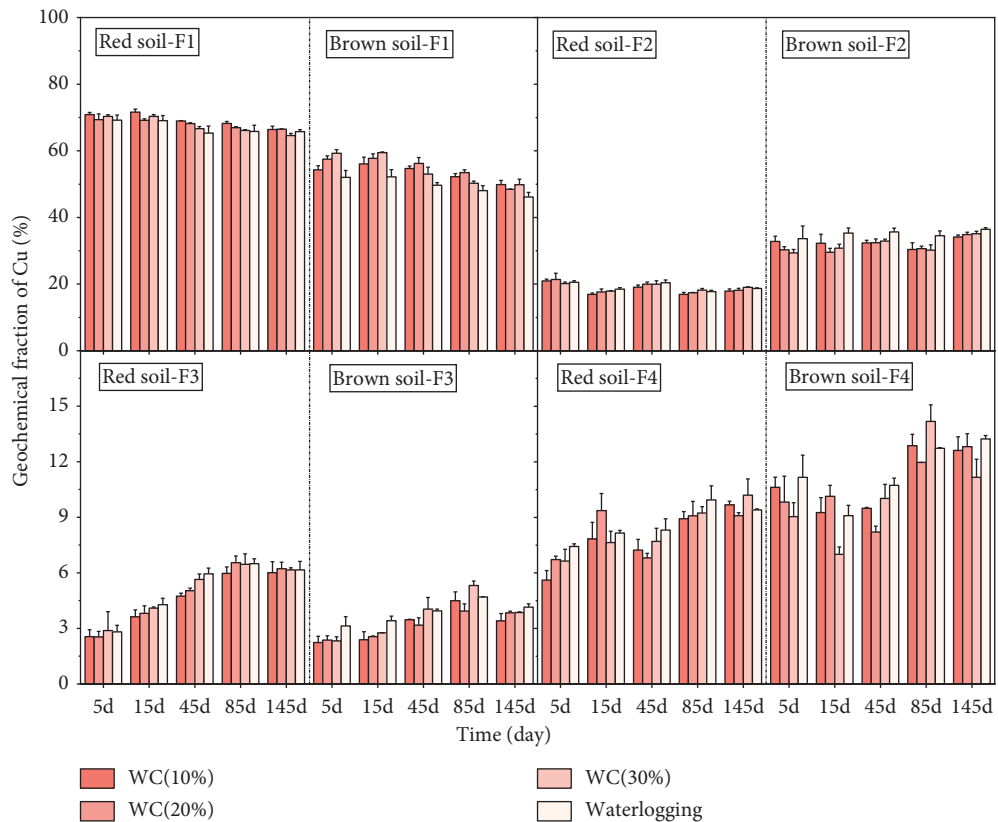

FIGURE 6: Changes of Cu fractions in different soil water contents as a function of contact time.
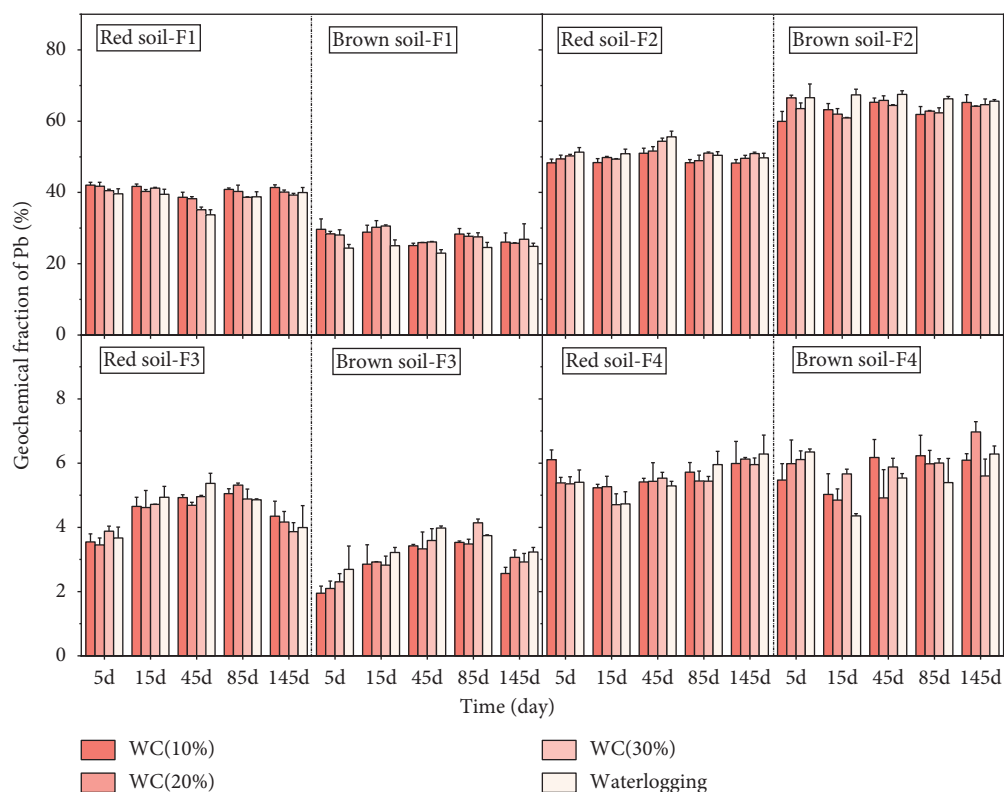
FIGURE 7: Changes of Pb fractions in different soil water contents as a function of contact time.

significant level for all cases. However, it can be found that, after 145 days of incubation, the proportions of F1 fraction of heavy metals were all lower for high water content experiments than low water content experiments. Conversely, the proportions of F2 fraction of heavy metals were all higher for high water content experiments. The results suggested that the water content of soils is one of the key factors of speciation redistribution of heavy metals after adding heavy metals. Change patterns of soil properties, such as Eh, pH, and Fe/Al oxides, are different under various water content, therefore induce the different change patterns of heavy metal speciation [20]. High soil water content can reduce oxygen diffusion and generate a reducing condition [46]. In addition, a part of Fe oxides can be dissolved under low Eh, and form less crystal Fe oxide, which possesses a high affinity for heavy metal ions [20, 47]. The processes of dissolution and recrystallization make heavy metals coprecipitation with Fe [48]. The formation of insoluble sulfide with heavy metals may be another cause of the reduction of F1 fraction under lower Eh [49]. Moreover, high water content during the aging experiment can increase soil pH [20]. With the increase in soil pH, the hydroxyl (-OH) groups of OM and metal oxides and carboxyl (-COOH) of OM can be converted to –COO⁻ and–O⁻, significantly increasing the negative charge [43, 45]. Moreover, high pH can result in an increase of adsorption and coprecipitation of heavy metals on metal oxides [50].

5. Conclusions

Aging of soil heavy metals is very significant for reducing their bioavailable fraction when heavy metals are discharged into the soil. In the present study, most introduced Cd, Cu, and Pb were transformed from soluble fraction to more stable fractions within 5 days of incubation, which was faster than other studies. Relatively lower concentrations of introduced heavy metals accounted for their rapid stabilization. The types of heavy metals and soils both affect the aging process. Based on the proportions of various fractions during incubation, it can be found that the transformation rate followed the order: Pb > Cu > Cd, and soil OM was the primary factor impacting the stabilization of soil heavy metals in the present study. During incubation, a higher proportion of F1 fraction of Cd and Cu and lower proportion of F2 fraction of Cd and Cu at 5°C and 10°C were observed than that at 25°C. Meanwhile, a lower proportion of F1 fraction of the heavy metals and a higher proportion of F2 fraction of the heavy metals were observed at waterlogged soil after incubation. The aging of soil heavy metals was accelerated under high temperature and soil water content. The result can contribute to assessing the environmental risk of soil heavy metal pollution.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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