

Effects of the Fe^{II}/Cu^{II} Interaction on Copper Aging Enhancement and Pentachlorophenol Reductive Transformation in Paddy Soil

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S Supporting Information

ABSTRACT: The present study investigated copper aging and pentachlorophenol (PCP) reductive transformation under the effects of the Fe^{II}/Cu^{II} interaction in paddy soil in south China. Kinetic measurements demonstrated that the PCP reductive transformation rate (*k*) could be promoted in the presence of no more than 0.375 mM Cu^{II} and inhibited in the presence of no less than 0.5 mM Cu^{II}. The highest *k* value in the presence of 0.25 mM Cu^{II} corresponds to the lowest redox potential (*E_p*) value of active Fe species. The increasing trend in *E_p* of the active Fe species is consistent with the declining trend in the *k* value of PCP reduction and vice versa. Dissolved Cu^{II} is gradually transformed into immobilized Cu species during PCP reduction, which indicates that Cu aging is enhanced by the Fe^{II}/Cu^{II} interaction. These findings improve our general understanding of the Fe^{II}/Cu^{II} interaction on soil iron redox chemistry for polychlorinated pesticide detoxification and heavy metal immobilization.

KEYWORDS: Pentachlorophenol, copper aging, Fe^{II}/Cu^{II} interaction, cyclic voltammetry, sequential extraction procedure

■ INTRODUCTION

Pentachlorophenol (PCP, C₆Cl₅OH) is a organic compound extensively used in agricultural, industrial, and domestic applications as an important component of fungicides, bactericides, herbicides, insecticides, molluscides, biocides, and wood preservatives.^{1,2} In China, PCP is commonly used in paddy soil to control snail-borne schistosomiasis and *Ampullaria gigas*. Despite the ban on the use of PCP in 1997, the adverse environmental effects of this compound will remain for a long period of time. This situation has attracted environmental concern because of the natural stability of PCP and its resistance to biodegradation.^{3–5} Generally, chemicals and microorganisms can be used to degrade and transform PCP into less harmful compounds through various techniques, such as electrochemical oxidation, photocatalytic degradation, etc.^{4–10} However, advanced oxidation processes are limited to treating contaminated soil or groundwater, which contains low concentrations of oxygen.¹¹ In the soil or rhizosphere, PCP degradation and transformation have been attracting much attention for the adverse effects of PCP on the environment and humans, which might last for a long time.^{12,13}

Iron (Fe) is the fourth most abundant element on the Earth's crust, and iron cycling in soil is important in the transformation of contaminants in soil environments.¹⁴ Previous studies reveal that surface-bound Fe^{II} formed on the interface of soil–water is a potential key factor in enhancing PCP transformation, and the reductive activity of surface-bound Fe^{II} in the dechlorination of PCP can be promoted effectively with polycarboxylic acids (oxalic, citric, succinic, and tartaric acids).^{14–18} The soils in south China, which developed under a subtropical monsoon climate, contain a large amount of free iron oxide with a special biogeochemistry. The dominant soil types, including Rhodic

Hapli–Udic Ferrosol, Plinthic Hapli–Udic Ferrosol, and Typic Hapli–Udic Ferrosol, in the subtropical and partly tropical Guangdong province of China contain more than 2% irons.¹⁹ As a result, the iron cycle has become an important energy source for geochemical processes of soil in this area. More importantly, Fe reduction is being actively used to stimulate the detoxification process of contaminated soils and is the main step of Fe species cycle in natural environments.^{14,15} Thus, the transformation of reducible pollutants may strongly depend upon the biogeochemistry of iron species.

Copper (Cu) is an essential trace element for plant growth and development. However, because of its heavy metal properties, the Cu content in soil should be controlled.^{20–22} Laboratory and field investigations have clearly demonstrated that the rates of contaminant reduction by Fe^{II} species can be promoted by adding Cu^{II}.^{23–26} Maithreepala and Doong^{23,24} investigated the effects of Cu in the dechlorination of carbon tetrachloride (CT) by Fe^{II}. Their study has revealed that Fe^{II} serves as the bulk reductant for both CT and Cu^{II}. The resulting Cu^I further acts as a catalyst to enhance the dechlorination rate of CT in iron-reducing environments. On the other hand, the chemical speciation, bioavailability, toxicity, and mobility features of Cu in soil have a significant correlation with a series of redox processes closely related to the redox process of iron in soil.^{23–25,27–32} Aging is defined as the process by which the extractability, bioavailability, and toxicity of Cu in soils decrease with time. This process has an important impact

Received: October 3, 2011

Revised: December 19, 2011

Accepted: December 19, 2011

Published: December 19, 2011

on the ecological risk assessment of copper in soils.^{29–31} Ma et al.^{29,30} developed a semi-mechanistic model to investigate the short-term (30 days) and long-term (2 years) aging of copper. Their study suggests that micropore diffusion is the main factor in the aging process of Cu. However, more direct evidence is needed to support copper aging in soils. Of significant interest to the current study is the course of Cu aging in soils under the interaction between Fe^{II} and Cu^{II}.

In recent years, sequential extraction procedure (SEP) methods have been originally developed to examine aquatic sediments. However, the SEP has gained wide acceptance as a tool for metal speciation in soils.³³ SEP has become a conventional method for the assessment of the bioavailability of heavy metals in soils and sediments, and it has been widely used to study Cu aging in soils.^{34,35} Cyclic voltammetry (CV) is a powerful electrochemical tool for studying the electrochemical behavior of active species on a solid electrode.^{16–18,26} Previous studies have clarified the effect of the Fe^{II}/Cu^{II} interaction on TiO₂ for 2-nitrophenol (2-NP) reductive transformation using the CV method. Results have shown that the declining trend in peak oxidation potential (E_p) of the active species is consistent with the increasing trend in the 2-NP reductive transformation rate and vice versa.²⁶ However, the use of SEP and electrochemical methods to study the effects of the Fe^{II}/Cu^{II} interaction on the reductive transformation of PCP as well as the course of Cu aging under the effect of the Fe^{II}/Cu^{II} interaction has been minimal.

In the present paper, experiments were performed in batch suspensions containing PCP, Cu^{II}, and paddy soil under various experimental conditions, such as sterile soil with and without different Cu^{II} concentrations and soil (non-sterile soil) with and without different Cu^{II} concentrations. The SEP method was used to extract and analyze Cu species. CV measurements were performed to identify the redox behavior of the active species. The objective of the current research was focused on clarifying the effect of the Fe^{II}/Cu^{II} interaction for PCP reductive transformation and Cu species transformation in paddy soil. Likewise, the present study aims to investigate the relationship among the kinetics of PCP transformation, electrochemical behavior of active species, and the effects of the Fe^{II}/Cu^{II} interaction.

MATERIALS AND METHODS

Soil Sampling. The soil sample (pH 4.74) was collected from Dongliangxia Village, Taishan City (22° 01.75' N, 112° 45.55' E) in south China. The parent material of the soil sample is littoral sediment, and the cation-exchange capacity (CEC) of the soils is 11.4 mol of cation/kg (+). The amount of organic matter (OM), K₂O, CaO, Na₂O, MgO, SiO₂, CuO, and Fe₂O₃ in the soil sample is 35.1, 15.4, 2.93, 5.29, 5.63, 640, 0.03, and 51.32 g/kg, respectively. The amount of iron species, including dithionite-extractable Fe (Fe_d), oxalate-extractable Fe (Fe_o), and pyrophosphate-extractable Fe (Fe_p), is 9.37, 6.29, and 1.28 g/kg, respectively. The soils, which were taken from the top layer of the field (0–15 cm), were air-dried and gently crushed prior to screening through a 2 mm sieve. The sieved soils were then stored at 4 °C prior to analysis and subsequent experiments.

Chemicals. The chemicals, which include 2-(*N*-morpholino)ethanesulfonic acid monohydrate (MES, >99.5%), PCP (98%), and lactic acid, were purchased from Sigma-Aldrich (Germany). CuCl₂·2H₂O (>98%) and methanol for high-performance liquid chromatography (HPLC) were purchased from Acros (Belgium). All chemicals were of analytical grade or higher and used without further purification.

Kinetic Studies. The typical reduction experiments were conducted in aqueous suspensions contained in 50 mL borosilicate

glass serum bottles with aluminum crimps and Teflon-lined butyl rubber septa using the same methods described in previous studies.²⁶ Experiments were conducted in an oxygen-free glovebox (Model Bactron II, Anaerobic Chamber, 200 plate capacity, Shellab, Shedon Manufacturing, Inc., Cornelius, OR) to prevent Fe^{II} oxidation. The glovebox atmosphere of 99.999% N₂ was continuously bubbled through 1 M NaOH solution to remove dissolved CO₂. Stock solutions of 0.03 M CuCl₂, 0.1 M MES, and 0.05 M lactic acid were prepared with reagent-grade water (18 MΩ cm resistivity, Milli-Q water). Stock solution of 1.0 mM PCP was dissolved in methanol in the oxygen-free glovebox and preserved in a dark-brown container. Solutions were filtered through a 0.2 μm filter prior to use. Suspensions prepared for the redox reactor contained 7.5 μM PCP, 0–1 mM CuCl₂, 50 mM MES, 10 mM lactic acid, and 1.25 g of soil. The total volume of the reaction suspension was 25 mL. Batch studies were conducted at pH 5.5. A constant suspension temperature of 30 ± 1 °C was achieved using a Bactron Anaerobic/Environment Chamber II (Shellab, Shedon Manufacturing, Inc., Cornelius, OR) and incubated in the dark. For the PCP kinetic studies, one of the 50 mL serum bottles was obtained from the equipment and transferred to the oxygen-free glovebox prior to routine analysis. After vigorous mixing, 3 mL of the suspension was taken out from the serum bottle and spiked with a water–ethanol mixture (50:50 volume). The suspension was immediately transferred to a 180 rpm horizontal shaker for 1 h. Afterward, the mixture was filtered with 0.45 μm syringe filters before conducting HPLC analysis. Additionally, another 2 mL of suspension was taken out from the serum bottle for Fe^{II} concentration analysis. The remaining 20 mL suspension in the serum bottle was used for Cu species analysis. All experiments were performed in triplicate and were replicated 3 times simultaneously.

Electrochemical Tests. The cyclic voltammograms were obtained using the methods described by Li et al.¹⁶ The electrochemical analyses were performed in a conventional three-electrode cell, equipped with the bare glassy carbon (GC) electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum spiral wire as the counter electrode. The cyclic voltammograms were recorded using an Autolab potentiostat (PGSTAT 30, Eco Chemie, The Netherlands) at a scan rate of 50 mV s⁻¹. The solution pH was adjusted with a diluted HCl or NaOH solution. High-purity N₂ gas was bubbled through the above electrolyte to remove dissolved oxygen.

Analyses. The PCP concentration was monitored via HPLC using the methods described by Lan et al.⁹ The mobile phase of the HPLC (Waters 1525/2487) with an Xterra C18 reverse-phase column was characterized by 1% acetic acid (HOAc) obtained in a solvent mixture of water and methanol with a ratio of 20:80 (v/v) at a flow rate of 1.0 mL min⁻¹. The column temperature was set to 35 °C, and an ultraviolet (UV) detector was used at 295 nm.

The pretreatment process of the PCP reductive transformation is described as follows. First, 25 mL of the sample was taken out to identify the intermediates of PCP anaerobic degradation. The sample was then extracted with ethanol for 1 h and separated after centrifugation. The sample was acetylated by reacting it with 2.5 mL of K₂CO₃ (0.7 mg/mL) and 2.5 mL of acetic anhydride. Afterward, 40 mL of hexane was extracted from the sample 4 times. The hexane layer was collected, dehydrated with anhydrous sodium sulfate, and concentrated to 0.5 mL. Then, the extract was purified with a neutral silica/alumina column and eluted with 80 mL of 70:30 (v/v) mixture of hexane and dichloromethane. Finally, the filtrate was concentrated to 0.5 mL using a rotary evaporator (N-1001, Shanghai Ailang Instruments Co., Ltd., Shanghai, Jiading, China) for gas chromatography–mass spectrometry (GC–MS) analysis. GC–MS analysis was performed using a gas chromatograph (Thermo Fisher Trace) equipped with a Thermo Fisher DSQ mass selective detector and capillary column (30 m × 0.24 mm × 0.25 μm, Thermo Fisher Scientific, Waltham, MA). The injector and ion source temperatures were 200 and 230 °C, respectively. The oven temperature was held at 55 °C for 2 min, increased to 160 °C at a rate of 15 °C/min, increased further to 250 °C at a rate of 15 °C/min, and maintained for 3 min.

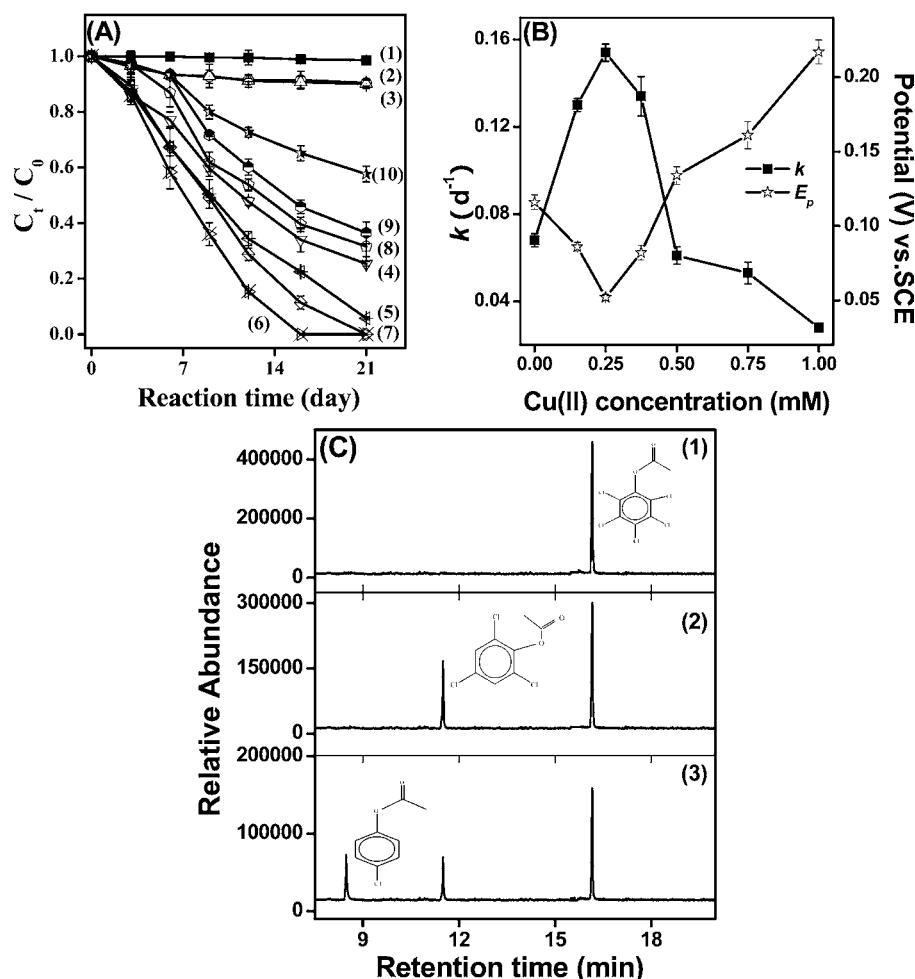


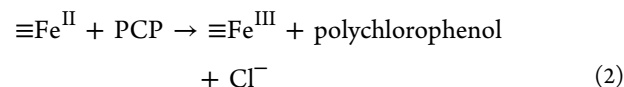
Figure 1. (A) PCP reductive transformation at pH 5.5 under different conditions. The conditions were as follows: (1) 0.5 mM Cu^{II} in homogeneous suspension, (2) sterile soil without Cu^{II} , (3) sterile soil with 0.5 mM Cu^{II} , (4) soil without Cu^{II} , (5) soil with 0.5 mM Cu^{II} , (6) soil with 0.25 mM Cu^{II} , (7) soil with 0.375 mM Cu^{II} , (8) soil with 0.5 mM Cu^{II} , (9) soil with 0.75 mM Cu^{II} , and (10) soil with 1 mM Cu^{II} . (B) Correlation among the k value of PCP reductive transformation, E_p value of the active species, and Cu^{II} concentration in soil suspensions. (C) GC-MS results of PCP reductive transformation in various conditions: (1) 0 days, (2) 9 days in soil without Cu^{II} , and (3) 9 days in soil with 0.25 mM Cu^{II} . Reaction conditions: 0–1.0 mM Cu^{II} , 10 mM lactic acid, 18.8 μM PCP, 50 mM MES, 50.0 g L^{-1} soil, and 298 K.

The Fe^{II} concentration was determined by the 1,10-phenanthroline method at 510 nm using a UV-vis spectrophotometer. The Cu^{II} species concentrations were determined using the SEP method with slight modifications.³³ All of the detailed procedures are described in section S1 of the Supporting Information.

RESULTS AND DISCUSSION

Effects of the Cu^{II} Concentration on PCP Reductive Transformation. A series of experiments was designed and conducted to investigate the effects of the Cu^{II} concentration on the reductive transformation of PCP under various conditions in sterile soil and soil (non-sterile soil), and the results are presented in Figure 1. No visible PCP transformation was detected upon the addition of Cu^{II} alone in homogeneous suspension without the addition of soil. This indicates that Cu^{II} species had no reductive activity in the reductive transformation of PCP. In either sterile soil suspensions without Cu^{II} or sterile soil suspensions with Cu^{II} , the heterogeneous reactions in soil suspensions proceeded with a faster rate than the homogeneous reactions because of the presence of active Fe^{II} species in soils.^{16,17,36–38} Previous studies^{14,15,39–43} have illustrated that reductive dissolution (RD) and dissimilatory Fe reduction (DIR) produce various

active Fe^{II} species [$\equiv\text{Fe}^{\text{II}}$] that accelerate the PCP reductive transformation rate in soil suspensions (eqs 1 and 2). Figure 1A indicates that PCP transformation generally follows the pseudo-first-order kinetics rate law. The rate constant (k) values were then obtained from the pseudo-first-order model fitting.



A set of experiments was performed with various Cu^{II} concentrations within the range of 0–1.0 mM to evaluate Cu^{II} effects on the reduction kinetics of PCP reductive transformation at a fixed pH value of 5.5 in soil suspensions. Notably, the PCP reductive transformation rate significantly increased with the increase in the Cu^{II} concentration from 0 to 0.25 mM. The rate continuously decreased with the increase in the Cu^{II} concentration above 0.25 mM. When the Cu^{II} concentration was modulated from 0 to 0.25 mM, the k value of PCP reductive transformation significantly increased from 0.068 ± 0.003 to $0.154 \pm 0.004 \text{ day}^{-1}$. The k value of PCP

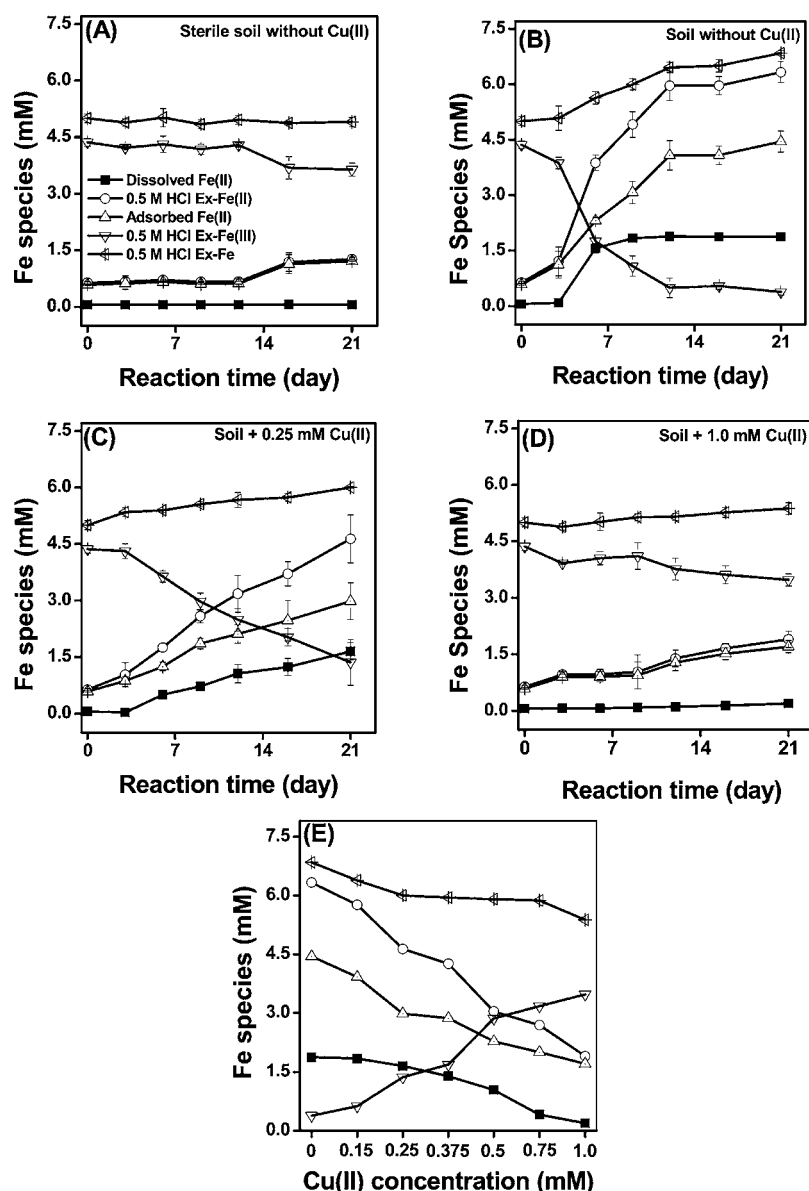


Figure 2. Fe species concentration in different conditions: (A) sterile soil without Cu^{II} , (B) soil without Cu^{II} , (C) soil with 0.25 mM Cu^{II} , and (D) soil with 1.0 mM Cu^{II} . (E) Fe species concentration with the increase in the Cu^{II} concentration in soil suspensions after 21 days. Reaction conditions were similar to those in Figure 1.

reductive transformation decreased to $0.028 \pm 0.002 \text{ day}^{-1}$ with the increase in the Cu^{II} concentration from 0.25 to 1.0 mM. The kinetic results indicate that the biggest k value of PCP reductive transformation was $0.154 \pm 0.004 \text{ day}^{-1}$ when the Cu^{II} concentration was 0.25 mM (Figure 1B).

GC-MS was used to identify the pathway of PCP reductive transformation, and the results are presented in Figure 1C. The GC-MS results indicate that tetrachlorophenol is neither present in soil suspensions without Cu^{II} nor present in soil suspensions with Cu^{II} . The analytical results of the production in soil suspensions without Cu^{II} show that 2,4,6-trichlorophenol is the only product from PCP reductive transformation after 9 days. In comparison, in soil suspensions with 0.25 mM Cu^{II} , 2,4,6-trichlorophenol and *p*-chlorophenol are the two primary intermediates from PCP reductive transformation in the same reaction time. The GC-MS results indicate that 2,4,6-trichlorophenol further transforms to *p*-chlorophenol under the effect of the $\text{Fe}^{\text{II}}/\text{Cu}^{\text{II}}$ interaction, which illustrates the

enhancing effect of the $\text{Fe}^{\text{II}}/\text{Cu}^{\text{II}}$ interaction on PCP reductive transformation.

Fe Species Variation during PCP Reductive Transformation. The present study proved that the amount of adsorbed Fe^{II} on the mineral surface is a crucial factor affecting the reduction rate of organic pollutants, as asserted in the literature.^{16–18,26,36–38} The different Fe species concentrations during PCP reductive transformation were investigated in various soil suspensions, and the results are shown in Figure 2. Excluding the effect of dissimilatory Fe reduction, the concentration of dissolved Fe^{II} , 0.5 M HCl Ex- Fe^{II} , adsorbed Fe^{II} , 0.5 M HCl Ex- Fe^{III} , and 0.5 M HCl Ex-Fe species in the original sterile soil sample without Cu^{II} were approximately 0.05, 0.6, 0.6, 4.4, and 5.0 mM, respectively (Figure 2A). In comparison to the various Fe species in sterile soil without Cu^{II} , the Fe species in soil without Cu^{II} were significantly different (Figure 2B). The concentration of dissolved Fe^{II} , 0.5 M HCl Ex- Fe^{II} , adsorbed Fe^{II} , and 0.5 M HCl Ex-Fe species increased

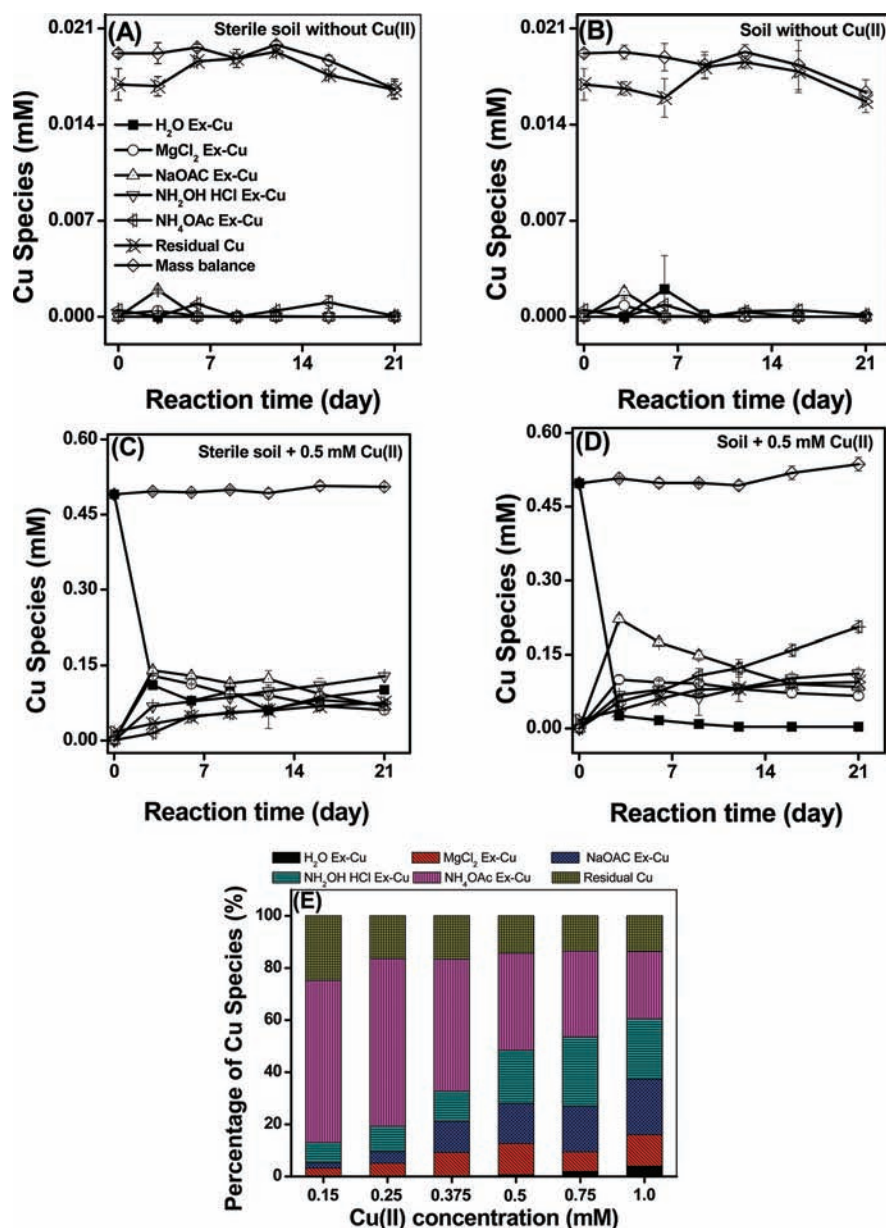


Figure 3. Cu species concentration in different conditions: (A) sterile soil without Cu^{II}, (B) soil without Cu^{II}, (C) sterile soil with 0.5 mM Cu^{II}, and (D) soil with 0.5 mM Cu^{II}. (E) Percentage of various Cu species with the increase in the Cu^{II} concentration in soil suspensions. Reaction conditions were similar to those in Figure 1.

with PCP dechlorination. The 0.5 M HCl Ex-Fe^{II} and adsorbed Fe^{II} concentrations increased from 0.6 to 6.3 mM and from 0.6 to 4.5 mM from 0 to 21 days, respectively. The results presented in Figure 2B indicate that the dissimilatory Fe reduction in soil increases the amount of active Fe^{II} species, which further accelerates the PCP dechlorination rate. In soil with 0.25 mM Cu^{II}, the concentration of dissolved Fe^{II}, 0.5 M HCl Ex-Fe^{II}, adsorbed Fe^{II}, and 0.5 M HCl Ex-Fe species increased, whereas the concentration of 0.5 M HCl Ex-Fe^{III} decreased with PCP reductive transformation, as indicated by five nearly straight lines (Figure 2C). With the increase in the Cu^{II} concentration from 0 to 1.0 mM, the increasing trends of dissolved Fe^{II}, 0.5 M HCl Ex-Fe^{II}, and adsorbed Fe^{II} and the decreasing trend of 0.5 M HCl Ex-Fe^{III} gradually slowed (panels C and D of Figure 2 and Figure S1 of the Supporting Information). Figure 2E shows the concentration of Fe species in soil suspensions after 21 days. The concentration of Fe^{II}

species decreased with the increase in the Cu^{II} concentration. In particular, the concentration of adsorbed Fe^{II} species decreased from approximately 4.45 to 1.7 mM, whereas the concentration of 0.5 M HCl Ex-Fe^{III} species increased from approximately 0.38 to 3.48 mM.

Yellow precipitates were found at the bottom of the serum bottle, which indicate the interaction between Fe^{II} and Cu^{II}.²⁶ Aqueous Cu²⁺ reacts with Fe²⁺ to form Cu₂O and ferrihydrite (eq 3), as proven by X-ray photoelectron spectroscopy (XPS), X-ray powder diffraction (XRPD), and Fourier transform infrared (FTIR) spectroscopy analysis.^{23,24} On the other hand, ≡Fe^{II} can serve as a reductant for adsorbed Cu^{II} [≡Cu^{II}], as described in eq 4.^{23,24} The trends of decreasing the Fe^{II} species concentration and increasing the Fe^{III} species concentration indicate that an increase in the Cu^{II} concentration results in a strong interaction between Fe^{II} and Cu^{II} and leads to a decrease in the amount of active Fe^{II} species, which slows the PCP

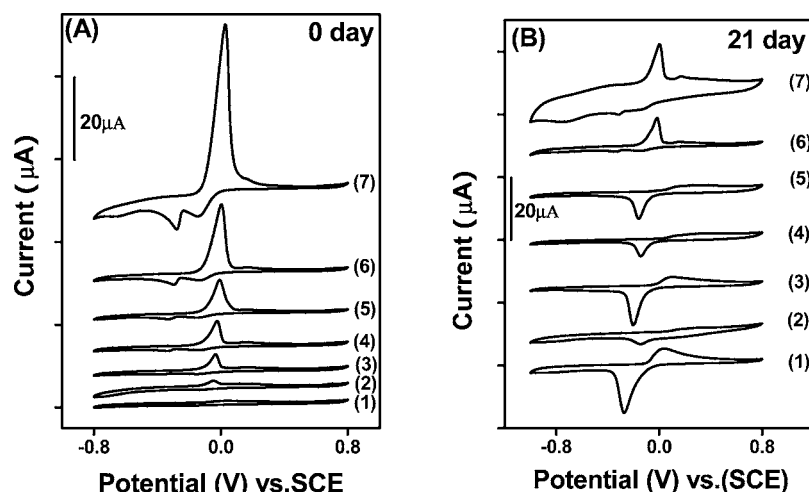
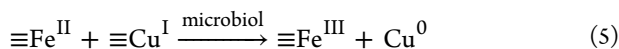
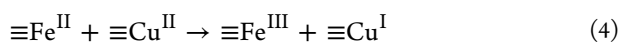
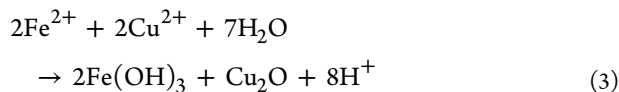


Figure 4. Cyclic voltammograms of active species on the bare GC electrode under various conditions after (A) 0 days and (B) 21 days. The conditions were as follows: (1) soil without Cu^{II} , (2) soil with 0.15 mM Cu^{II} , (3) soil with 0.25 mM Cu^{II} , (4) soil with 0.375 mM Cu^{II} , (5) soil with 0.5 mM Cu^{II} , (6) soil with 0.75 mM Cu^{II} , and (7) soil with 1 mM Cu^{II} . Electrochemical measurements were conducted in the cell (25 mL) containing 0–1.0 mM Cu^{II} , 7.5 μM PCP, 50 mM MES, 50.0 g L^{-1} soil, and 10 mM lactic acid at 298 K. The solution pH was 5.5, and the scan rate was 50 mV s^{-1} .

reductive transformation rate.²⁶ Maithreepala and Doong^{23,24} found that the resulting Cu^{I} can further act as a catalyst to enhance the dechlorination rate of CT in iron-reducing environments. However, the dechlorination of PCP by Cu^{I} was not significantly detected in our experimental conditions. Moreover, under the effect of microbes in soils, $\equiv\text{Fe}^{\text{II}}$ may also serve as a reductant that reacts with the available $\equiv\text{Cu}^{\text{I}}$ to form Cu^0 that accelerates the process of copper aging (eq 5). These studies are currently underway.



Cu Species Transformation during PCP Reduction.

Figure 3 shows the concentration of different Cu species in various soil suspensions. The background concentrations of the various Cu species were much lower and stable whether in sterile soil or in soil suspensions without Cu^{II} (panels A and B of Figure 3), which can be neglected in the investigation of Cu species transformation. A set of experiments was performed in sterile soil suspensions and in soil suspensions to evaluate the effect of the $\text{Fe}^{\text{II}}/\text{Cu}^{\text{II}}$ interaction on the variation in Cu species at a fixed Cu^{II} concentration of 0.5 mM, as shown in panels C and D of Figure 3. Figure 3C shows that the decreasing trends of easily extractable Cu species (i.e., H_2O Ex-Cu, 1 M MgCl_2 Ex-Cu, and 1 M NaOAc Ex-Cu) and the increasing trends of non-easily extractable Cu species (i.e., 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ Ex-Cu, 3.2 M NH_4OAc Ex-Cu, and residual Cu) were not significant. Moreover, the concentration of each Cu species was hardly indistinguishable in sterile soil suspensions with 0.5 mM Cu^{II} , indicating the slow rate of Cu species transformation in sterile soil suspensions. In contrast, the decreasing trends of easily extractable Cu species as well as the increasing trends of non-easily extractable Cu species were significant in soil suspensions with 0.5 mM Cu^{II} (Figure 3D), especially the increase in the concentration of 3.2 M NH_4OAc Ex-Cu (metal

bound to OM). This observation demonstrates that the $\text{Fe}^{\text{II}}/\text{Cu}^{\text{II}}$ interaction enhances Cu species transformation and reveals the important role of Fe^{II} in reductive transformations of Cu in soil suspensions.

With an increased reaction time, the concentration of soluble Cu^{II} (H_2O Ex-Cu) rapidly decreased. The concentration of metal bound to iron and manganese oxides (0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ Ex-Cu), metal bound to OM, and residual Cu increased with the increase in the reaction time (Figure S2 of the Supporting Information). Figure 3E shows the percentage of various Cu species in soil suspensions after 21 days. Notably, with the increase in the Cu^{II} concentration from 0 to 0.25 mM, the concentration of exchangeable Cu species was much lower, especially the concentration of dissolved Cu species, which was almost negligible. The concentrations of Cu species bound to OM and residual Cu species were much higher. In soil with 0.25 mM Cu^{II} , the percentage of each Cu species was 0, 4.8, 4.2, 9.2, 60.7, and 15.5%. The percentage of Cu species bound to OM and residual Cu species continuously decreased, whereas the concentration of other Cu species increased with the increase in the Cu^{II} concentration above 0.25 mM. For instance, when the Cu concentration increased from 0.25 to 1.0 mM, the percentage of easily extractable Cu species and those bound to Fe–Mn oxides were increased to 4.1, 12.3, 21.8, and 23.6%. The percentage of Cu species bound to OM and residual Cu species were decreased to 26.4 and 13.9%, respectively. The dissimilatory Fe reduction in soil increased the amount of Fe^{II} species, which accelerated the $\text{Fe}^{\text{II}}/\text{Cu}^{\text{II}}$ interaction in soil (Figure 2). The results shown in Figure 3 reveal that the effect of the $\text{Fe}^{\text{II}}/\text{Cu}^{\text{II}}$ interaction promotes the ease in extractability of Cu species in soils and prove that the $\text{Fe}^{\text{II}}/\text{Cu}^{\text{II}}$ interaction enhances Cu aging.^{26,44,45}

Electrochemical Behaviors of Active Species on the Soil-Modified Electrodes. Cyclic voltammograms using homemade mineral-modified electrodes were performed to evaluate the electron transfer behavior of adsorbed $\text{Fe}^{\text{II}}/\text{Cu}^{\text{II}}$ species, which can prove the redox potential change.²⁶ Figure 4 illustrates the redox behavior of surface-complex $\text{Fe}^{\text{II}}/\text{Cu}^{\text{II}}$ species on bare GC electrodes at 0 days. All of the voltammograms, except for soil without Cu^{II} , clearly exhibited

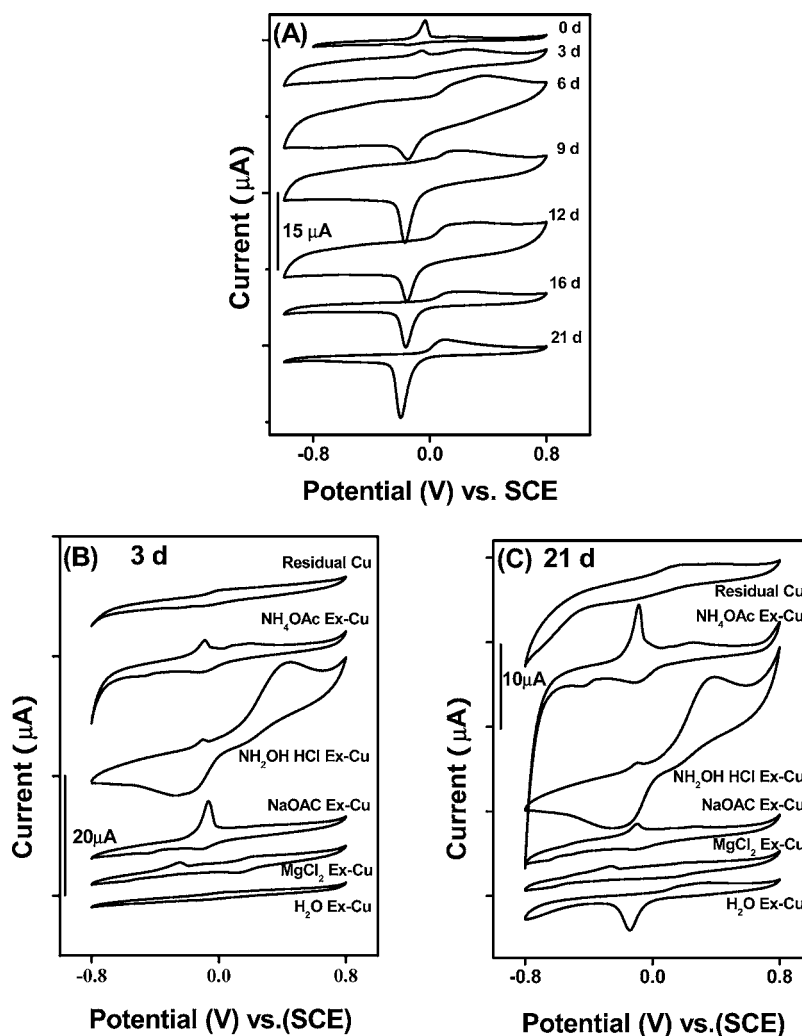


Figure 5. (A) Cyclic voltammograms of active species on the bare GC electrode under different reaction times in soil with 0.25 mM Cu^{II} suspensions. Cyclic voltammograms of different Cu species on the bare GC electrode after (B) 3 days and (C) 21 days. Electrochemical measurements were similar to those in Figure 4.

a pair of peaks: an anodic oxidation peak for the reduction state approximately at a potential ranging from -0.1 to 0.2 V (versus SCE) and a cathodic reduction peak for the oxidation state at a potential ranging from -0.3 to 0 V (versus SCE). The peak height and intensity of the anodic oxidation peak increased with the increase in the Cu^{II} concentration (0 – 1.0 mM) in soil suspensions (Figure 4A).

In soil suspensions without Cu^{II} , the CV results (Figure 4B and Figure S3 of the Supporting Information) indicated that, under the effects of the dissimilatory Fe reduction, the amount of Fe^{II} species increased and the E_p of Fe^{II} adsorbed onto the bare GC electrode was approximately 0.05 V (versus SCE). With the increase in the Cu^{II} concentration, in soil suspensions with 0.5 mM Cu^{II} , the CV results (Figure S3 of the Supporting Information) showed that the anodic oxidation peak of adsorbed Cu^{II} species sharply decreased with the increase in the reaction time, which almost disappeared after 9 days. A similar behavior was observed in other soil suspensions with different Cu^{II} concentrations. The reduced peak height and intensity of the anodic oxidation peak indicated the extent of the reaction between Fe^{II} and Cu^{II} , which was intensified with the increase in the reaction time and Cu^{II} concentration.²⁶

The correlation among the k value of PCP reductive transformation, E_p value of the active species, and Cu^{II} concentration in soil suspensions was also investigated. Results are shown in Figure 1B. The results indicate that a negative correlation exists between k values of 2-NP transformation and E_p values of the active species with the increase of the Cu^{II} concentration from 0 to 1.0 mM. When the Cu^{II} concentration is between 0 and 0.25 mM, the E_p value of the active species significantly decreases from 0.116 ± 0.005 to 0.052 ± 0.002 V (versus SCE). The E_p value of the active species significantly increases from 0.052 ± 0.002 to 0.217 ± 0.008 V (versus SCE) when the Cu^{II} concentration continuously increases from 0.25 to 1.0 mM. Correspondence with the largest k value of PCP transformation ($0.154 \pm 0.004 \text{ day}^{-1}$) when 0.25 mM Cu^{II} is added produces the lowest E_p value [0.052 ± 0.002 V (versus SCE)]. The increasing trend in E_p of the active species is consistent with the declining trend in k values of PCP reductive transformation and vice versa.

Cu Aging Enhanced by the $\text{Fe}^{\text{II}}/\text{Cu}^{\text{II}}$ Interaction. The Cu species transformation under the effects of the $\text{Fe}^{\text{II}}/\text{Cu}^{\text{II}}$ interaction was investigated by designing and conducting CV experiments to investigate the active species using the SEP method, and the results are presented in Figure 5. In soil with

0.25 mM Cu^{II} (Figure 5A), under the effects of dissimilatory Fe reduction, the CV results showed that the peak height and peak intensity of the anodic oxidation peak gradually decreased, whereas the peak height and peak intensity of a new anodic oxidation peak at approximately 0.2 V (versus SCE) gradually increased with the increase in the reaction time. Similar results were observed in soil with other different Cu^{II} concentrations, and the results are shown in Figure S4 of the Supporting Information. Panels B and C of Figure 5 show the CV results of different Cu species in soil suspensions with 0.25 mM Cu^{II} using the SEP method. No significant signals corresponding to dissolved Cu, exchangeable Cu, and residual Cu species were detected. The increase in the reaction time, peak height, and peak intensity of Cu species bound to carbonates were decreased, whereas the peak height and peak intensity of Cu species bound to Fe–Mn oxides were increased, which was similar to the trend of Cu species bound to OM.

In Figures 4 and 5, the CV results clearly indicated the decrease in Cu^{II} species with the increase in the reaction time, whereas an increase in active species was observed at potential values of approximately 0.2–0.4 V (versus SCE). In comparison to the CV results of Cu species in soil suspensions using the SEP method, the reduced peak height and peak intensity at approximately 0 V (versus SCE) indicated the decreased amount of dissolved, exchangeable, and carbonate-bound Cu species. In comparison, the increased peak height and peak intensity at approximately 0.32 V (versus SCE) indicated the increased amount of Fe–Mn-oxide-bound and OM-bound Cu species. These results corresponded with the results shown in Figure 3 and Figure S2 of the Supporting Information and indicated the aging of Cu under the effects of dissimilatory Fe reduction with the increase in the reaction time.

The present study clarified the enhancement of Cu aging and reductive transformation of PCP on a paddy soil under Fe^{II}/Cu^{II} interaction effects. The kinetic results demonstrate that the PCP reductive transformation rate significantly increases with the increase in the Cu^{II} concentration from 0 to 0.25 mM and then decreases with the increase in the Cu^{II} concentration from 0.25 to 1.0 mM. Under varied Cu^{II} concentrations, CV tests proved that the increasing trend in E_p of the active species is consistent with the declining trend in k values of PCP reductive transformation and vice versa. On the other hand, the results of the SEP method indicate the trends of easily extractable Cu species transformed to non-easily extractable Cu species together with PCP reductive transformation, revealing that Cu aging is enhanced by the effects of the Fe^{II}/Cu^{II} interaction. Although the concentrations of Cu^{II} used in the present study were higher than in naturally available Cu^{II}, the results obtained are expected to improve our general understanding of the Fe^{II}/Cu^{II} interaction on soil iron redox chemistry. Likewise, the findings will provide positive implications for detoxification of polychlorinated pesticides and immobilization of heavy metal ions.

■ ASSOCIATED CONTENT

● Supporting Information

Data analyses (sections S1–S6), Fe (Figure S1) and Cu (Figure S2) species concentrations in different conditions, cyclic voltammograms of active species on the bare GC electrode in soil suspensions under various conditions (Figure S3), and cyclic voltammograms of active species on the bare GC electrode under different reaction periods in soil suspensions

(Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Funding

This work was financially supported by the National Natural Science Foundation of China (Grants 41001136 and 41025003), the Natural Science Foundation of Guangdong Province for Doctoral Scientific Research Program (Grant 10451065003005011), the Youth Science Foundation of Guangdong Province Academy of Sciences (Grant qnj201002), the “973” Program (Grant 2010CB134508), and the Guangzhou Technology Support Project (Grant 2009Z1-E541).

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