

Effects of methamidophos and glyphosate on copper sorption-desorption behavior in soils

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Abstract A batch-equilibration technique was employed to study the impact of two organo-phosphorus pesticides methamidophos (MDP) and glyphosate (GPS) on copper (Cu^{2+}) sorption-desorption for phaeozem and burozem collected from Northeastern China. The addition of the two pesticides decreased Cu^{2+} sorption, increased Cu^{2+} desorption and prolonged the equilibrium time of Cu^{2+} sorption-desorption. But GPS appeared to exert a stronger influence on Cu^{2+} sorption-desorption due to its stronger complexation with Cu^{2+} . When MDP was added, Cu^{2+} sorption-desorption was linearly correlated with MDP treatment concentrations. But in the presence of GPS, Cu^{2+} sorption first underwent a rapid decrease period, and then slowly tended towards a steady period. The reverse pattern could be found for Cu^{2+} desorption in the presence of GPS. Without pesticides and with the existence of MDP, Cu^{2+} sorption-desorption kinetics was well conformed to two-constant equation and Elovich equation. But that was not the case for Cu^{2+} desorption kinetics in the presence of GPS although its sorption could be also described by these two equations.

Keywords: Cu, sorption, desorption, methamidophos, glyphosate, phaeozem, burozem.

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Soils contaminated by copper (Cu) often pose a high risk to ecosystem safety and human health^[1]. In the northeast China, Cu pollution often occurs in soils receiving repeated application of pig dung (as farm manure) that contains high Cu. It has been reported that Cu in these pig dung reached as high as 1990 mg • kg⁻¹^[2]. Cu-containing fungicides have been widely used in greenhouses and agricultural fields and also contributed to the increased soil Cu concentration^[3]. In addition, many large thermal power plants in this area have been built up to produce sufficient electric and heat energy for cold winter, and as a result, the fly ash containing Cu from coal combustion in the

fire-power plants will become point-source of Cu when it finally deposits in the soil^[4]. The increase of Cu concentration in soil potentially lowered soil productivity and water quality of the area. Cu concentration in soil solution is generally controlled by sorption-desorption and/or dissolution-precipitation processes^[5]. Many ligands presented in soil, such as humic acid, organic acids, pesticides, and other organic pollutants, can form metal-ligand complexes with Cu and thus affect Cu sorption-desorption behavior^[6], and ultimately the migration of Cu in soil/water interface or leaching to groundwater. It is necessary to understand Cu behavior in soil environment in relation to

complex ligands that are commonly used in agriculture, especially organic pesticides.

Insecticide methamidophos (MDP) has been widely used in China. In 1990, the application of MDP reached 35000 tons, greater than any other pesticides^[7]. Glyphosate (GPS), a non-selective, broad-spectrum, post emergent herbicide extensively used in agriculture, frequently mixes with bordeaux (Cu sulfate and lime) as fungicide for controlling mildew. These pesticides can form complexes with Cu and thus potentially affect solubility and bioavailability of Cu in soil and the environment.

Some studies have investigated the effects of GPS on Cu²⁺ sorption. Wang et al.^[8] reported that GPS reduced Cu²⁺ sorption on Ca-montmorillonite by complexing with Cu²⁺, while increased Cu²⁺ sorption on δ -Al₂O₃ through "bridge" bonding with δ -Al₂O₃. Maqueda et al.^[9] found that Cu²⁺ sorption on the M-FA (a natural fulvic acid complex) increased with increasing GPS, for the formation of GPS complexes with Al and Fe in solution created vacant sorbing sites on M-FA surface, and thus facilitated Cu²⁺ sorption. Morillo et al.^[6,10,11] pointed out that free Cu²⁺ in soil solution would be drastically reduced at the presence of GPS because of the complexing reaction between Cu²⁺ and GPS, and Cu sorption decreases generally with increasing GPS concentration in solution, principally due to the lower equilibrium pHs. For the same pH values, the influence of GPS on Cu²⁺ sorption mainly depended on soil sorption capability for Cu²⁺, and the presence of GPS probably enhanced Cu²⁺ sorption if the soil had a greater capability to sorb it^[6]. However, there were fewer reports regarding the effects of MDP on Cu²⁺ sorption-desorption in soil environment.

In this study, we compared the influences of two organophosphorus pesticides, MDP and GPS, on Cu sorption-desorption in typical soils of northeast China:

phaeozem and burozem. The results obtained in this work should lead to a better understanding of Cu retention processes by soils in the presence of organophosphorus pesticides, and provide a scientific basis for preventing combined pollution between heavy metals and pesticides.

1 Materials and methods

1.1 Tested materials

Two unpolluted soils (phaeozem and burozem) were sampled at the 0—20 cm depth. Phaeozem was collected from the Hailun Agro-ecological Trial Station, in Hailun County of Heilongjiang Province, China; and burozem was collected from the Shilihe Agro-ecological Trial Station in Shenyang of Liaoning Province, China. The fresh soil samples were air-dried, sieved to <0.5 mm. Soil pH was measured in a 5 : 2 water/soil ratio using a pH meter. Soil organic matter (OM) was determined using a C-N autoanalyzer (Model 1500 Carlo Erba, Japan). Soil total Cu (1 : 4 HNO₃/HClO₄ digestion), available Cu (0.1 N HCl extraction) and the concentration of Cu in the digester and extracts were measured using the atomic absorption spectrometry (AAS, Hitachi 180-80, Japan). The cation exchange capacity (CEC) was determined using 1.0 mol/L NH₄OAC extraction. Soil texture was determined by the gravimeter method^[12]. Some important properties of the soils studied are shown in table 1.

The MDP (O, S-Dimethyl phosphoroamidothiolate, CH₃SCH₃OPONH₂) is a broad-spectrum pesticide. Pure MDP is a colorless crystalline solid with melting point 44.5°C^[13]. The emulsified oil containing 40% MDP (pH 6.37) was used in this study, purchased from Zhejiang Industry University Chemical Plant (Hangzhou, Zhejiang Province). Pure GPS (N-2 phosphonomethyl glycine, (HO)₂OPCH₂NHCH₂COOH) is

Table 1 Some soil properties

Soil type	pH (water)	OM(%)	CEC/cmole • kg ⁻¹	Total Cu/mg • kg ⁻¹	Available Cu/mg • kg ⁻¹	Silt (%) 0.05—0.001 mm	Clay (%) <0.001 mm
Phaeozem	6.48	3.98	32.92	12.67	3.14	67.09	29.02
Burozem	6.09	2.31	19.23	13.37	7.79	75.59	17.10

a high efficient and nontoxic herbicide with melting point 230°C ^[13]. The GPS tested in this study was 10% GPS salt solution (pH 6.12), manufactured by the Jiangan Chemical Plant in Jiangsu Province, China.

1.2 Sorption and desorption experiments

A batch-equilibration technique, using 1.00 g soil and 20 mL solution containing 0.01 mol/L CaCl_2 , $80 \text{ mg} \cdot \text{L}^{-1} \text{Cu}^{2+}$ and different concentrations of MDP or GPS in a 100 mL polyethylene centrifuge tube, was employed to study the sorption of Cu^{2+} in the above two soils. Calcium chloride (0.01 mol/L) was used as the background solution, instead of water, because the electrolyte composition in 0.01 mol/L CaCl_2 is similar to that of soil solutions near field capacity moisture conditions. Three replicate samples were analyzed for all the experiments. Each tube of the batch samples that contains 1.0000 g soil was treated with either MDP at the concentrations of 0, 100, 200, 400, 800, or $1200 \text{ mg} \cdot \text{L}^{-1}$, respectively, or GPS at the concentrations of 0, 10, 20, 50, 100, 200, 500, 1000, 1500, or $2500 \text{ mg} \cdot \text{L}^{-1}$, respectively at the $80 \text{ mg} \cdot \text{L}^{-1} \text{Cu}^{2+}$ concentration. The suspension was shaken for 24 h in an orbital shaker ($25 \pm 1^{\circ}\text{C}$), then was centrifuged for 5 min at $10000 \times g$, and the supernatant was filtered through moderate-speed filter paper. The concentration of Cu^{2+} in the filtrate was measured using the AAS. Another experiment was conducted to observe the effects of time on Cu^{2+} sorption in the presence or absence of MDP or GPS. The concentrations of MDP and GPS were $600 \text{ mg} \cdot \text{L}^{-1}$ and $100 \text{ mg} \cdot \text{L}^{-1}$, respectively at the presence of $80 \text{ mg} \cdot \text{L}^{-1} \text{Cu}^{2+}$, and the equilibrium time intervals were 1, 2, 5, 10, 15, 20, 40, 80, 120, and 240 min, respectively. The rest was the same as the above experiments.

For the desorption experiment, 1.0000 g soil and 20 mL solution containing 0.01 mol/L CaCl_2 and $80 \text{ mg} \cdot \text{L}^{-1} \text{Cu}^{2+}$ were placed into each centrifuge tube, and the suspension was shaken for 2 h ($25 \pm 1^{\circ}\text{C}$). After 24 h ($25 \pm 1^{\circ}\text{C}$), the suspension was centrifuged, filtered, and 20 mL supernatant solution were removed for Cu^{2+} analysis. Desorption was initiated by immediate addition of 10 mL 0.01 mol/L CaCl_2 containing 0,

100, 200, 400, 800, $1200 \text{ mg} \cdot \text{L}^{-1}$ MDP or 0, 10, 20, 50, 100, 200, 500, 1000, 1500, $2500 \text{ mg} \cdot \text{L}^{-1}$ GPS. The suspensions were shaken for 24 h ($25 \pm 1^{\circ}\text{C}$), centrifuged, and then the aqueous phase from the test tube was removed for Cu^{2+} determination. For the kinetic study, the experiment was conducted in the similar way: samples of 1.0000 g soil and 10 mL 0.01 CaCl_2 containing $80 \text{ mg} \cdot \text{L}^{-1} \text{Cu}^{2+}$ and MDP at 0 or $600 \text{ mg} \cdot \text{L}^{-1}$, or GPS at 0 or $100 \text{ mg} \cdot \text{L}^{-1}$ were placed in each centrifuge tube and were equilibrated for 1, 2, 5, 10, 15, 20, 40, 80, 120, 240 min, respectively.

The amount of sorbed Cu^{2+} in the soils was calculated as the difference between the initial Cu^{2+} and equilibrium Cu^{2+} concentration. The amount of Cu^{2+} desorbed from the Cu-enriched soils was calculated as the difference between the equilibrium Cu^{2+} concentration after desorption and the equilibrium Cu^{2+} concentration before desorption.

2 Results

2.1 Primary soil properties related to Cu^{2+} sorption and desorption behavior

Soil pH, cation exchange capacity (CEC), and organic matter content are the major soil properties that affect Cu^{2+} sorption by soils. In this study, phaeozem had a greater cation exchange capacity ($32.92 \text{ cmol} \cdot \text{kg}^{-1}$) than burozem ($19.23 \text{ cmol} \cdot \text{kg}^{-1}$) due to its higher organic matter content (table 1). Organic matter content in phaeozem was 1.72 times higher than that in burozem. Both soils were slightly acid, but pH of phaeozem was slightly higher than that of burozem. In relation to the size particle distribution, phaeozem contained a higher clay content, and burozem had a slightly higher content of silt fraction.

2.2 Thermodynamics of Cu^{2+} sorption with the addition of MDP and GPS

Addition of MDP led to a slight decrease of Cu^{2+} sorption, and sorbed Cu^{2+} was linearly correlated with MDP concentrations (fig. 1(a)). MDP resulted in a bigger reduction in sorbed Cu^{2+} for burozem than for phaeozem. When the added concentration of MDP was $1200 \text{ mg} \cdot \text{L}^{-1}$, sorbed Cu^{2+} in burozem was decreased

by 4.83%, as compared with 3.37% in phaeozem.

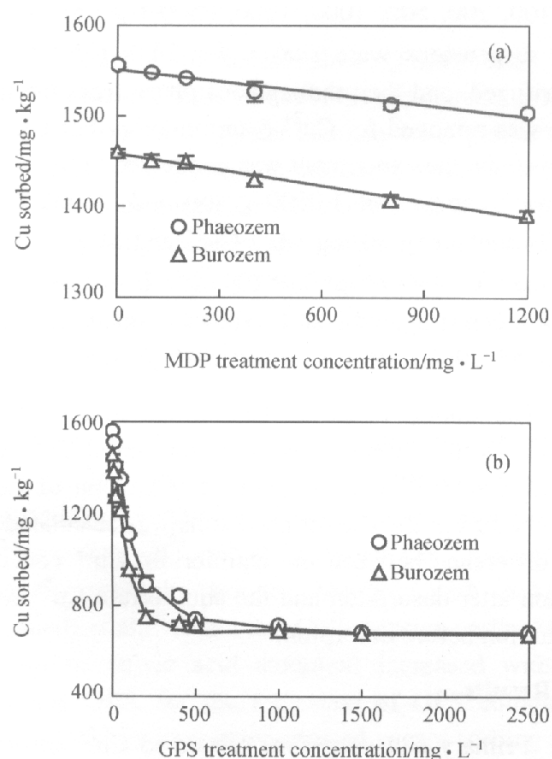


Fig. 1. Effects of methamidophos (MDP) (a) and glyphosate (GPS) (b) on sorbed Cu²⁺ in 80 mg · L⁻¹ Cu²⁺ solution by phaeozem and burozem (25°C).

GPS addition induced more obvious reduction in Cu²⁺ sorption compared with MDP (fig. 1(b)). When GPS concentration ranged from 0 to 500 mg · L⁻¹ in phaeozem and from 0 to 200 mg · L⁻¹ in burozem, the decline of Cu²⁺ sorption was dramatic. As GPS continuously increased, Cu²⁺ sorption began to slowly decrease. At 1500 mg · L⁻¹, sorbed Cu²⁺ on phaeozem

and burozem were almost reduced to the same minimum (sorbed Cu²⁺ decreased by 52.57% and 50.50% for phaeozem and burozem, respectively), but almost leveled off at higher GPS concentrations.

In order to precisely evaluate the impact of MDP and GPS on Cu²⁺ sorption-desorption behavior in soils, the partition coefficient K_p (L · kg⁻¹), which is the ratio of equilibrium Cu²⁺ concentration in the soil to that in the aqueous phase, was calculated using the equation:

$$K_p = C_s/C_e, \quad (1)$$

where C_s (mg · kg⁻¹) and C_e (mg · L⁻¹) are the amounts of sorbed Cu²⁺ by the soil and equilibrium Cu²⁺ concentration, respectively.

K_p values have been frequently used to assess the extent of sorption-desorption of metals and their potential mobility. The lower the K_p value, the less sorption the metal. In the Cu²⁺ sorption process, the value of K_p for phaeozem was almost 4 times higher than that for burozem without the pesticides (tables 2 and 3). The data suggests that the extent of Cu²⁺ sorption reaction on phaeozem is far bigger than on burozem.

In the presence of pesticides, the increase of MDP concentration gradually declined K_p values for Cu²⁺ sorption. But with the existence of GPS, the K_p value firstly underwent an abrupt decrease period at GPS concentrations of 0–500 mg · L⁻¹ for phaeozem and 0–200 mg · L⁻¹ for burozem, respectively, and then slowly tended towards a steady value of about 15 for both soils.

Table 2 K_p for Cu²⁺ sorption/desorption in phaeozem and burozem with methamidophos (MDP) concentrations

Concentration/mg · L ⁻¹	Sorption		Desorption	
	phaeozem	burozem	Phaeozem	Burozem
0	860.38 ± 29.60*	220.97 ± 5.33	1297.86 ± 26.45	442.29 ± 6.27
100	723.37 ± 12.90	204.13 ± 11.78	1227.17 ± 25.71	374.02 ± 4.59
200	621.67 ± 8.60	196.76 ± 13.00	1139.72 ± 18.93	350.86 ± 5.85
400	545.85 ± 5.57	178.99 ± 2.43	1093.90 ± 7.50	334.19 ± 8.34
800	383.83 ± 11.58	153.83 ± 7.35	981.77 ± 8.00	283.41 ± 7.60
1200	341.43 ± 15.26	135.89 ± 0.91	918.84 ± 13.03	256.69 ± 3.81

* Standard deviation.

Table 3 K_p for Cu^{2+} sorption/desorption in phaeozem and burozem with glyphosate (GPS) concentrations

Concentration/ $\text{mg} \cdot \text{L}^{-1}$	Sorption		Desorption	
	phaeozem	burozem	phaeozem	burozem
0	857.59 ± 29.08	215.70 ± 7.05	1274.86 ± 32.47	443.41 ± 10.70
10	375.41 ± 11.22	131.26 ± 1.82	458.28 ± 5.39	126.95 ± 2.27
20	148.66 ± 14.22	80.17 ± 1.67	224.02 ± 0.57	75.40 ± 5.96
50	110.48 ± 4.83	64.24 ± 2.26	168.79 ± 4.29	60.93 ± 2.56
100	45.59 ± 0.47	28.75 ± 1.51	93.15 ± 1.09	33.02 ± 1.47
200	25.31 ± 2.17	17.65 ± 1.04	47.98 ± 2.85	25.06 ± 1.66
400	22.27 ± 1.05	16.39 ± 0.42	28.47 ± 4.58	21.44 ± 2.36
500	17.20 ± 1.02	16.21 ± 0.28	21.33 ± 0.12	19.29 ± 0.07
1000	16.07 ± 0.32	15.20 ± 0.61	21.34 ± 0.06	19.25 ± 0.04
1500	14.96 ± 0.28	14.77 ± 0.23	21.65 ± 0.22	19.13 ± 0.05
2500	14.97 ± 0.29	14.57 ± 0.31	21.71 ± 0.06	19.45 ± 0.23

2.3 Thermodynamics of Cu^{2+} desorption with the addition of MDP and GPS

Cu^{2+} desorption with increasing concentrations of MDP or GPS is presented in fig. 2. Without pesticides, Cu^{2+} desorbed from phaeozem and burozem accounted for only 0.66% and 1.75% of initial Cu^{2+} sorption, respectively.

Contrary to Cu^{2+} sorption process, a significant positive correlation was found between desorbed Cu^{2+} and MDP concentrations for both soils (fig. 2(a)). At the maximum of MDP concentration employed in the experiment ($1200 \text{ mg} \cdot \text{L}^{-1}$), only 1.00% and 3.43% of the sorbed Cu^{2+} were desorbed from phaeozem and burozem, respectively (fig. 2(a)).

GPS addition remarkably increased Cu^{2+} desorption from the soils compared with MDP, and the isotherm curve of Cu^{2+} desorption for phaeozem was almost identical to that for burozem (fig. 2(b)). When GPS concentration ranged from 0 to $500 \text{ mg} \cdot \text{L}^{-1}$, desorbed Cu^{2+} was rapidly increased to the maximum of $497 \text{ mg} \cdot \text{kg}^{-1}$ for phaeozem and $491 \text{ mg} \cdot \text{kg}^{-1}$ for burozem, and about 31.87% and 33.66% of the sorbed Cu^{2+} were desorbed from the two soils, respectively. But with the GPS concentration further increasing, Cu^{2+} desorption was difficultly reduced again (fig. 2(b)).

Similar to Cu^{2+} sorption process, the presence of MDP and GPS also dramatically decreased K_p values

for Cu^{2+} desorption (tables 2 and 3). In the presence of GPS, K_p value was acutely decreased when GPS concentrations ranged from 0 to $500 \text{ mg} \cdot \text{L}^{-1}$, and it should be noted that K_p value stayed about 21.4 for phaeozem and 19.3 for burozem at GPS concentrations of $500 \text{ mg} \cdot \text{L}^{-1}$ or higher.

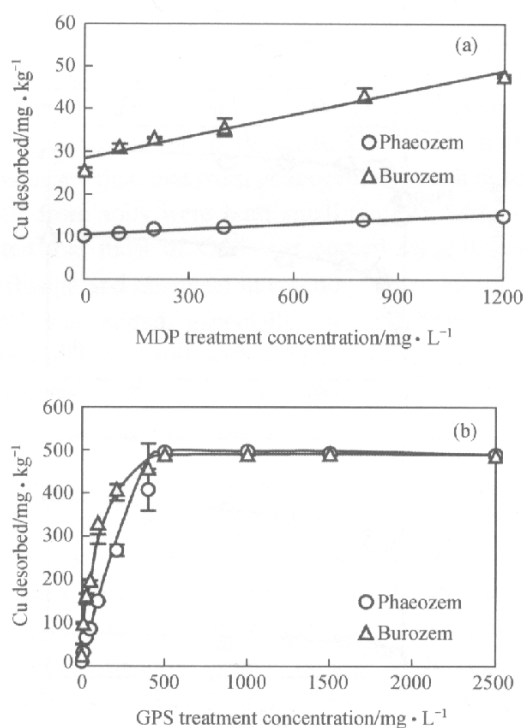


Fig. 2. Effects of MDP (a) and GPS (b) on desorbed Cu^{2+} in $80 \text{ mg} \cdot \text{L}^{-1}$ Cu^{2+} solution by phaeozem and burozem (25°C).

2.4 Kinetics of Cu^{2+} sorption with the addition of MDP and GPS

The kinetics of Cu^{2+} sorption by phaeozem and burozem with or without MDP or GPS are shown in fig. 3. The Cu^{2+} sorption consisted of two-stage reaction, an initially rapid sorption, and followed by a slower one regardless of MDP or GPS presence. The rapid reaction is most probably ascribable to chemical reaction and film-diffusion processes, and the slower one has been attributed to diffusion into micropores of inorganic minerals and humic components, sites of lower reactivity and surface precipitation^[14]. The Cu^{2+} sorption without the pesticides was extremely rapid, with >98% of Cu^{2+} sorption occurring within only 1 min for the two soils (fig. 3(a)). But Cu^{2+} sorption in the presence of MDP and GPS had a longer rapid

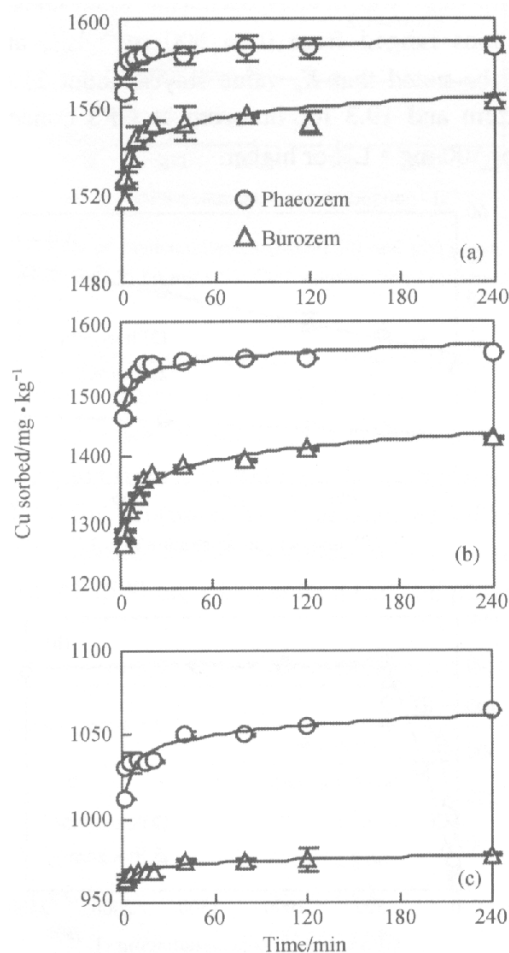


Fig. 3. Time course of sorbed Cu^{2+} in $80 \text{ mg} \cdot \text{L}^{-1}$ Cu^{2+} solution by phaeozem and burozem in the absence (a) and presence of $600 \text{ mg} \cdot \text{L}^{-1}$ MDP (b) and $100 \text{ mg} \cdot \text{L}^{-1}$ GPS (c) in the soil suspension (25°C).

sorption stage. At the $600 \text{ mg} \cdot \text{L}^{-1}$ MDP, 90% of the Cu^{2+} sorption occurred within 1 and 2 min for phaeozem and burozem, but 10 and 120 min for the soils to complete 98% of the Cu^{2+} sorption, respectively (fig. 3(b)). At the presence of $100 \text{ mg} \cdot \text{L}^{-1}$ GPS, it took 1 min to achieve 98% of Cu^{2+} sorption in burozem, but took 1 and 40 min for phaeozem to achieve 90% and 98% of the Cu^{2+} sorption, respectively (fig. 3(c)).

Two-constant equation and Elovich equation are often used to simulate the chemical kinetics process:

$$\ln Y = A + B \ln t, \quad (2)$$

$$Y = A + B \ln t, \quad (3)$$

where t is time (min), A and B are model constants, Y is the sorbed/desorbed Cu^{2+} ($\text{mg} \cdot \text{kg}^{-1}$). The two equations best described the Cu^{2+} sorption in both two soils regardless of the presence of pesticides ($P < 0.001$) (tables 4 and 5), but the Cu^{2+} sorption obeyed the two-constant equation better than Elovich equation because of the smaller S_e .

2.5 Kinetics of Cu^{2+} desorption with the addition of MDP and GPS

Fig. 4 shows the kinetics of Cu^{2+} desorption from phaeozem and burozem. Without pesticides, 95% of Cu^{2+} desorption took about 20 min (fig. 4(a)), but took about 80 min in the presence of MDP (fig. 4(b)). In these two cases, Cu^{2+} desorption was well conformed to the two-constant equation and Elovich equation ($P < 0.001$) (tables 4 and 5). It should be noted that GPS addition changed the pattern of Cu^{2+} desorption kinetics, and the process would be hardly described by the above simple equations. With the existence of GPS, desorbed Cu^{2+} was rapidly raised and reached the maximum, respectively at 10 min on burozem and 15 min on phaeozem, and then slowly decreased until about 120 min (fig. 4(c)).

3 Discussion

Previous studies indicated that the forces involved in heavy metal sorption by soil range from weak, physical, van der Waals forces (e.g. partitioning) and electrostatic outer-sphere complexes (e.g. ion exchange) to chemical interactions^[14]. Chemical interac-

Table 4 Correlative coefficients (r) and standard errors (S_e) of two-constant equation for Cu^{2+} sorption/desorption in the presence or absence of MDP and GPS by soils (25°C)

Process	Soil	Cu		Cu+MDP		Cu+GPS	
		r	S_e	r	S_e	r	S_e
Sorption	Phaeozem	0.8929***	0.0019	0.9250***	0.0007	0.9411***	0.0052
	Burozem	0.9482***	0.0030	0.9867***	0.0067	0.9775***	0.0012
Desorption	Phaeozem	0.8814***	0.0182	0.8787***	0.0127	–	–
	Burozem	0.9600***	0.0801	0.9686***	0.0159	–	–

* Standard error S_e and correlative coefficient r were used to judge whether the equation conform to the model. The bigger is r and the smaller is S_e , the better is the model.

Table 5 Correlative coefficients (r) and standard errors (S_e) of Elovich equation for Cu^{2+} sorption/desorption in the presence or absence of MDP and GPS by soils (25°C)

Process	Soil	Cu		Cu+MDP		Cu+GPS	
		r	S_e	r	S_e	r	S_e
Sorption	Phaeozem	0.8937***	3.0045	0.9279***	12.4296	0.9502***	5.0642
	Burozem	0.9490***	4.5803	0.9890***	7.8774	0.9773***	1.1950
Desorption	Phaeozem	0.8790***	0.2221	0.9572***	0.2250	–	–
	Burozem	0.9618***	0.8336	0.9848***	0.4227	–	–

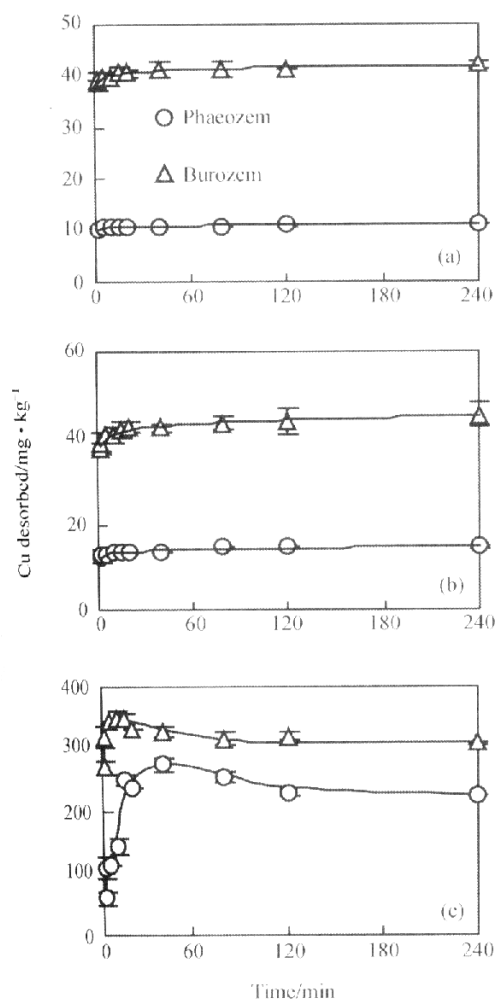


Fig. 4. Time course of desorbed Cu^{2+} in $80 \text{ mg} \cdot \text{L}^{-1}$ Cu^{2+} solution by phaeozem and burozem in the absence (a) and presence of $600 \text{ mg} \cdot \text{L}^{-1}$ MDP (b) and $100 \text{ mg} \cdot \text{L}^{-1}$ GPS (c) in the soil suspension (25°C).

tions involved ligand exchange mechanism, covalent bonding, hydrogen bridges, and steric or orientation effects^[15]. When Cu^{2+} enters into soil, it is quickly fixed by the soil and transformed into three forms: partitioning Cu^{2+} , ion exchanging Cu^{2+} and chemical interacting Cu^{2+} . The partitioning Cu^{2+} is most readily desorbed from soil, whereas the chemical interacting Cu^{2+} is very difficult to release from the soil particle. In our experiments, the data obtained from thermodynamics of Cu^{2+} desorption showed that, without pesticides, the quantity of desorbed Cu^{2+} from burozem was larger than that from phaeozem although desorbed Cu^{2+} from soils were both small (fig. 2), which indicated that most of Cu^{2+} was sorbed on soils by ion exchange and chemical interactions when $80 \text{ mg} \cdot \text{L}^{-1}$ Cu^{2+} was added, especially on phaeozem, because phaeozem is a soil with a high concentration of organic matter and clay that provide a greater sorption surface than burozem (table 1).

Previous studies indicated that pesticides affect heavy metal sorption by competing for sorption sites or complex reaction^[16]. It has been reported that the complex reaction is the major mechanism when GPS reacts with Cu^{2+} ^[17–19]. In the molecule of GPS, there are three function groups (amine, carboxylate and phosphonate) forming strong coordination bonds with Cu^{2+} to give complexes^[17]. The GPS-Cu complexes probably have four forms: CuG^- , CuHG , CuH_2G^+ and $\text{CuH}_3\text{G}^{2+}$ (G presents the ligand of GPS)^[6]. Which

GPS-Cu complex form takes advantageous position? It depends on equilibrium pH of soil solution. In our study, pH values of phaeozem (pH 6.48), burozem (pH 6.09) and GPS salt solution (pH 6.12) are all slightly acidic, therefore, CuHG and CuH_2G^+ could be the dominant GPS-Cu complexes. As far as the electrovalence of GPS-Cu complex was concerned, CuHG and CuH_2G^+ have the lower tendency to be sorbed than free Cu^{2+} . This may be the main reason why the addition of GPS can inhibit Cu^{2+} sorption and facilitate Cu^{2+} desorption.

The study of electron spin resonance indicated that, when GPS reacts with Cu^{2+} , the amine-N in the GPS molecule combines with Cu^{2+} at first, followed by carboxylate-O and phosphonate-O^[20]. However, few studies have indicated what kind of reaction occurs when MDP is mixed with Cu^{2+} . According to Dong^[21] and Huang^[22], complexing reaction was the most likely mechanism between them. Amine-N in MDP molecule may combine with Cu^{2+} to form M-Cu complex (M presents the ligand of MDP). The lower polarity of MDP may account for its lower binding with Cu^{2+} and MDP only had a smaller effect on Cu^{2+} sorption-desorption.

The change of K_p value well reflected the impacts of these two pesticides on Cu^{2+} sorption-desorption. The lower K_p showed the higher probability of Cu migration in the presence of the pesticides. Evidently, GPS addition posed the higher risk of Cu^{2+} pollution compared with MDP.

In the kinetics of Cu^{2+} sorption-desorption experiments with the existence of GPS, Cu^{2+} desorption was not exactly the reverse process of Cu^{2+} sorption. The possible reason was that the reactions among GPS, Cu^{2+} , GPS-Cu, sorbed Cu^{2+} and other heavy metal ions of soil solution in Cu^{2+} sorption experiment were different from that in Cu^{2+} desorption experiment. In the sorption process, Cu^{2+} and GPS were simultaneously added to the centrifuge tubes, so that the complex reaction between GPS and Cu^{2+} as well as Cu^{2+} sorption reaction simultaneously happened. Under the concentrations of GPS and Cu^{2+} used in the experiments, Cu^{2+} was excessive (the ratio of added GPS

molar concentration to added Cu^{2+} molar concentration was 1 : 2.13), and thus the whole Cu^{2+} sorption was the sum of free Cu^{2+} sorption and GPS-Cu complexes sorption. So GPS addition did not change the model of Cu^{2+} sorption kinetics (fig. 3(a) and (c)). In the desorption experiments, excessive GPS was added to soils enriched with high contents of sorbed Cu^{2+} . The GPS firstly chelated with Cu^{2+} fixed on soils through the van der Waals forces and some weak chemical bonds, which resulted in the rapid desorption of Cu^{2+} at the first 40 and 10 min for phaeozem and burozem, respectively. As the concentration of GPS-Cu complexes increased in soil solution, the cross-linked reaction among GPS, GPS-Cu, and other heavy metal ions in soil solution may inevitably occur, resulted in Cu^{2+} desorption slowly dropping off after reaching the maximum (fig. 4(a) and (c)).

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