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Effect of Methamidophos on Sorption–Desorption Behavior of Copper in Soils

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Copper (Cu) is an essential micronutrient for plants, but it is also a potentially toxic element that can be deposited on soils from Cu fertilizers, Cu fungicides, sewage sludge, coal slag and polluted water from copper smelting (He et al., 1998; Sun et al., 2001). Soils contaminated with Cu often pose a high risk to ecosystem safety and human health (Song et al., 2002).

In northeast China, animal dung and powdered firing coal contribute to most of the Cu accumulation in the soil environment. In intensive pig farming, forage containing $CuSO_4$ is often used to accelerate the rate of the pig's growth (Zhen, 1999). It was reported that the Cu content of pig dung was as high as 1990 mg kg^{-1} when forage containing $CuSO_4$ was fed (He et al., 1998). Cu pollution happened with the application of this pig dung as organic fertilizer to the soil near the intensive pig farm. In addition, many thermal power plant and coal-fired boilers were built to provide electricity and heat energy during the cold winters in this area. The powdered firing coal produced by coal combustion often floats in the air and finally falls on the soil near city and town dwellings. Qu (1997) discovered that the Cu content in powdered firing coal was up to 155 mg kg^{-1}. The powdered firing coal piled up near the thermal power plants and coal fired boilers will certainly expose crops and humans to Cu toxicity.

Sorption-desorption of Cu is one of the primary processes that affects the fate and mobility of Cu in soils (Zhou, 1995; Scheidegger et al., 1996). Several researchers have described the Cu sorption and desorption process. Soil pH, cation exchange capacity (CEC), and organic matter content are important parameters that affect Cu sorption by soils (Harter, 1979; Harter, 1983; Mclaren et al., 1981). The concentration of Cu in soil solutions is influenced by sorption-desorption reactions of Cu with various soil colloidal materials (Mclaren et al., 1973; Quirk et al., 1975). Cu sorption-desorption firstly undergoes a rapid reaction, and is then followed by a slow reaction (Benjamin et al., 1981). There was a distinct hysteresis between sorption and desorption isotherms (Yang et al., 1998).

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Many pesticides applied in the soils inevitably influence the environmental behavior of heavy metal. Several studies have investigated the mutual impact of pesticides and heavy metals on each other. Mortland and Raman (1967) discovered that the Cu^{2+} ion was the most efficient catalyst for some organic phosphate pesticides degradation; Diazinon and Chlorpyrifos were decomposed rapidly when touching Cu^{2+}-montmorillonite. Wang (1996) reported that Glyphosate obviously reduced the sorption of Cu on Ca-montmorillonite by complexion with Cu^{2+} ions, while increased the Cu sorption on δ-Al_2O_3 through "bridge" bonding with δ-Al_2O_3, and Chlordimeform decreased the Cu sorption on Ca- montmorillonite through competing for the sorption sites with Cu^{2+} ions.

Methamidophos as a highly efficient pesticide had been widely used in the cropland of China. In 1990, the application of methamidophos had reached to 35000 tons, the amount of which gave first priority to the other pesticides (Hua et al., 1996). The addition of Methamidophos may exert significant influence on the ultimate fate of Cu. The objective of this study was to evaluate the effect of methamidophos on copper sorption and desorption in typical soils of northeast China—Phaeozem and Burozem, and provide evidence for preventing combined pollution between heavy metal and methamidophos.

MATERIALS AND METHODS

Unpolluted surface soils (0~20 cm) were sampled from two sites. The first site is Hailun agricultural ecology trial station, in Hailun county of Heilongjiang Province, China; the second one, Shilihe agricultural ecology trial station, in Shenyang city of Liaoning Province, China. The fresh soil samples were air-dried, and sieved to <4.5mm. Soil pH was measured in water at a 2:5 ratio of soil solution. Organic matter (O.M.) was determined by dry combustion (C-N autoanalyzer 1500 Carlo Erba). Soil total Cu, available Cu and the concentration of Cu in the above extractants were measured by atomic absorption spectrometry (Hitachi 80-180, Japan). The cation exchange capacity (CEC) was determined by 1.0M NH_4OAC extraction (Thomas, 1982). Soil texture was determined by gravitometer (Li, 1983). Some important properties of soils studied are shown in Table 1.

Methamidophos (O,S-Dimethyl phosphoroamido thiolate, $(CH_3S)(CH_3O)PONH_2$, Monitor®, Tamaron®) is a broad-spectrum pesticide. Methamidophos is a colorless crystalline solid of melting point 44.5℃. The emulsified oil containing 40% methamidophos (pH: 6.37) used in this study was purchased from Ruize Pesticide Corporation (Shandong Province, China).

A batch-equilibration technique, using 1.0000 g soil and 20 ml solution containing 0.01 M $CaCl_2$, 80 mg L^{-1} Cu^{2+} and different concentration of methamidophos was employed to study the sorption of Cu^{2+} by the above soils. Calcium chloride (0.01 M) was used as background solution, instead of water, because the electrolyte composition in 0.01 M $CaCl_2$ is similar to that of soil solutions near field capacity moisture conditions. Three replicate samples were analyzed in every experiment.

Table 1. Physical and chemical properties of the soils studied

Soils	pH	O.M. (%)	CEC (cmol kg^{-1})	Total Cu (mg kg^{-1})	Available Cu (mg kg^{-1})	Texture (%)	
						Silt	Clay
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

Every 100-ml polyethylene centrifuge tube with 1.0000 g soil was treated with methamidophos concentrations of 0, 100, 200, 400, 800, 1200 mg L^{-1} respectively under the 80 mg L^{-1} Cu^{2+} concentration. The suspension was shaken for 24 hr in an orbital shaker (25℃), then was centrifuged for 5 min at 5000×g, and the supernatant was filtered though middle-speed filter paper. The concentration of Cu^{2+} in the filtrate was measured by using the atomic absorption spectrometry. Another experiment was conducted to observe the effects of time on Cu^{2+} sorption in the presence and absence of methamidophos. The initial treatment of Cu^{2+} was 80 mg L^{-1}, methamidophos were 0, 600, 1200 mg L^{-1} respectively, and shaking time were 1, 2, 5, 10, 15, 20, 40, 80, 120, 240 min respectively, the rest was the same as the above experiments.

As for the desorption, 1.0000 g soil and 20 ml solution containing 0.01 *M* $CaCl_2$ and 80 mg L^{-1} Cu^{2+} were put into the centrifuge tubes, and the suspension was shaken for 2 hr (25℃), after about 16 hr (25±1℃), the suspension was centrifuged, filtered, and 20 ml supernatant were removed for Cu^{2+} analysis. Desorption was initiated by immediate addition of 10 ml methamidophos (0, 100, 200, 400, 800, 1200 mg L^{-1}) containing 0.01 M $CaCl_2$. The samples were shaken for 24 hr (25℃), 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 same way with the following exceptions: samples of 1.0000 g soil and 80 mg L^{-1} Cu^{2+}, methamidophos (0, 600, 1200 mg L^{-1} respectively) in the centrifuge tube were reacted for 1, 2, 5, 10, 15, 20, 40, 80, 120, and 240 min.

Sorbed Cu^{2+} by soil was calculated as the difference between the initial Cu^{2+} and equilibrium Cu^{2+} concentrations. Cu^{2+} desorbed by the soil was calculated as the difference between the equilibrium Cu^{2+} concentration after desorption and the equilibrium Cu^{2+} concentration before desorpion. The calculations are:

$$S=V_1(C_0-C_1)/W \tag{1}$$

$$D=(V_2C_2-R^*C_1)/W \tag{2}$$

Where S was sorbed Cu^{2+} (mg kg^{-1}); D was desorbed Cu^{2+} (mg kg^{-1}); C_0 was Cu^{2+} treatment concentration (80 mg L^{-1}); C_1 was equilibrium Cu^{2+} concentrations during the sorption process (mg L^{-1}); C_2 was equilibrium Cu^{2+} concentrations during the desorption process (mg L^{-1}); R was the weight of residual liquid (g); W was soil weight (g); and as well as V_1 and V_2 were the volume per centrifuge tube of the sorption and desorption process respectively (ml).

RESULTS AND DISCUSSION

Sorption of Cu^{2+} was decreased with the increase of methamidophos in solution of two soils (Figure 1). A significant negative correlation (P=0.01 level) was found between sorbed Cu^{2+} and methamidophos concentration. So the linear equation $S=aM+b$ (where S is sorbed Cu^{2+}, M is methamidophos in solution, a is decrease in rate of Cu^{2+} sorption, and b is sorbed Cu^{2+} without methamidophos) was used to simulate the relationship between Cu^{2+} sorption and methamidophos concentration. Regression equations for phaeozem and burozem were: $S=-0.0662M+1550.6$ ($R^2=0.9646$), $S=-0.1467M+1437.3$ ($R^2=0.9937$), respectively. According to the two equations, sorbed Cu^{2+} was decreased more quickly on burozem than on phaeozem with an increase of methamidophos in solution when 80 mg L^{-1} of Cu^{2+} was added.

The kinetics of Cu^{2+} sorption by phaeozem and burozem are shown in Figure 2. The Cu^{2+} initially underwent a rapid sorption reaction, followed by a slower reaction. Sorption of Cu^{2+} without methamidophos was extremely rapid, with >98% of Cu^{2+} sorption occurring within only 1 min for the two soils. But the sorption of Cu^{2+} in the presence of methamidophos had a longer rapid sorption reaction. When the methamidophos concentrations were 600 and 1200 mg L^{-1}, 95% of Cu^{2+} sorption respectively took 5 and 10 min on phaeozem, however, 90% of Cu^{2+} sorption respectively took about 80 and 120 min on burozem. The addition of methamidophos decreased the Cu^{2+} sorption rate, and delayed the equilibrium time of Cu^{2+} sorption: the more methamidophos in the solution, the longer the equilibrium time of Cu^{2+} sorption. Meanwhile, it took more time to reach the Cu^{2+} sorption equilibrium on burozem than it did on phaeozem with the presence of methamidophos.

The experimental data from the Cu^{2+} sorption were applied to several commonly used kinetic models. We employed first-order equation and two-constant kinetic equation, as well as Elovich equation and Parabolic diffusion equation, to model the experimental Cu^{2+} sorption data (Table 2). Elovich equation, two-constant equation and first-order equation all perfectly described the sorption of Cu^{2+} on the two soils in the presence or absence of methamidophos, but the two-constant equation was the best. The addition of methamidophos did not essentially change the kinetic model of Cu^{2+} sorption on the two soils.

Desorption of Cu^{2+} was inversely related to the amount sorbed Cu^{2+} by the two soils. Without the presence of methamidophos, Cu^{2+} desorbed from the two soils respectively accounted for only 0.74% and 2.09% of the amount sorbed Cu^{2+} (Figure 3), which indicated that, when 80 mg L^{-1} of Cu^{2+} was added, most of Cu^{2+} was so tightly fixed by the two soils that it re-entered the soil solution with difficulty, especially on phaeozem.

The addition of methamidophos accelerated Cu^{2+} desorption (Figure 3). There was a significant positive correlation (P=0.001 level) between desorbed Cu^{2+} and methamidophos concentration. So the linear equation $D=cM+e$ (where D is desorbed Cu^{2+}, M is methamidophos in solution, c is the increase in rate of Cu^{2+} desorption, and e is desorbed Cu^{2+} without methamidophos) can be perfectly used to model the relationship between desorbed Cu^{2+} and methamidophos

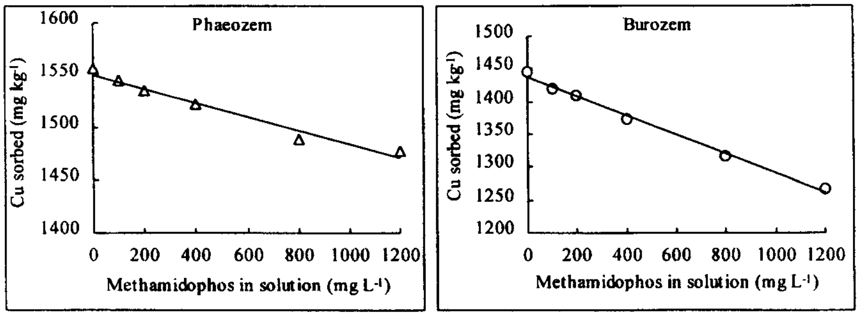

Figure 1.Cu^{2+} sorption on phaeozem and burozem in the presence of methamidophos with initial 80 mg L^{-1} Cu^{2+} treatment.

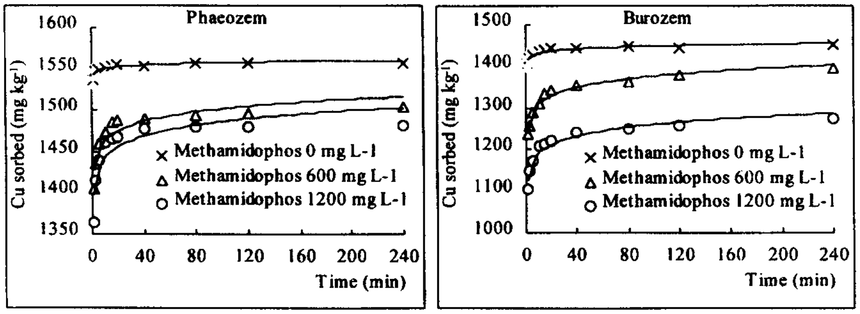

Figure 2.Cu^{2+} sorption on pheaozem and burozem with initial 80 mg L^{-1} Cu^{2+} treatment.

concentration. Regression equations for phaeozem and burozem were: D=0.0037M+12.44 (R^2=0.9651), D=0.0152M+34.05 (R^2=0.9575), respectively. The increase in rate of Cu^{2+} desorption (c) for burozem was 4 times as high as that for phaeozem, which indicated that Cu^{2+} desorption from burozem was more easily accelerated by methamidophos than that from phaeozem.

Figure 4 shows the kinetics of Cu^{2+} desorption by phaeozem and burozem. Cu^{2+} desorption was slow compared with the sorption reaction and not completely reversible during the 240 min desorption experiment. Cu^{2+} desorption firstly underwent a rapid reaction, followed by a slow reaction. A greater quantity of Cu^{2+} (>90%) was desorbed from the two soils during the first 40 min whether methamidophos was added or not. The addition of methamidophos decreased the Cu^{2+} desorption rate, and delayed the equilibrium time of Cu^{2+} desorption. Without methamidophos, 95% of Cu^{2+} desorption occurred within the first 20 min for the two soils, but it took about 80 min to reach 95% of Cu^{2+} desorption in the presence of methamidophos.

Several commonly used kinetic models, first-order equation and two-constant kinetic equation, Elovich equation and Parabolic diffusion equation, were used to model the kinetic of Cu^{2+} desorption (Table 3). The results showed that Cu^{2+}

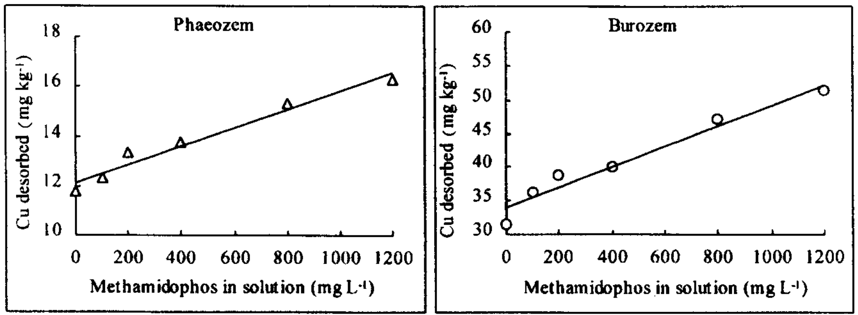

Figure 3.Cu^{2+} desorption on phaeozem and burozem in the presence of methamidophos with initial 80 mg L^{-1} Cu^{2+} treatment.

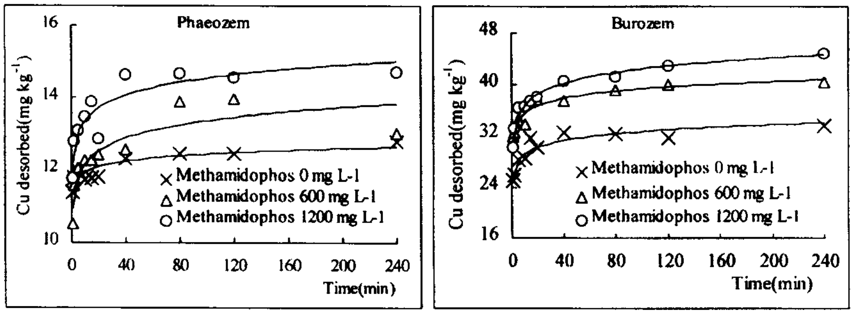

Figure 4.Cu^{2+} desorption on phaeozem and burozem with initial 80 mg L^{-1} Cu^{2+} treatment.

desorption experimental data from phaeozem perfectly fitted to the Elovich equation and the two-constant equation; and those from burozem perfectly fitted to the Elovich equation, the two-constant equation and the first-order equation whether methamidophos was added or not. But the two-constant equation best described the kinetic of Cu^{2+} desorption, and methamidophos addition did not essentially change the kinetic model of Cu^{2+} desorption from the two soils.

The above results showed that, methamidophos obviously decreases sorbed Cu^{2+}, increases desorbed Cu^{2+}, and delays Cu^{2+} sorption and desorption equilibrium time. The significant impacts of methamidophos on Cu^{2+} sorption and desorption are not the consequence of the change of soil solution pH. According to our experiment, the addition of methamidophos slightly raised soil solution pH with an initial 80 mg L^{-1} Cu^{2+} treatment.

There may be three possible reasons to explain this phenomenon when methamidophos was added into soils with Cu^{2+}: (a) a protonation happened as methamidophos' amide ($-NH_2$) changed to $-NH_3^+$, which resulted in a sorption site competition between positive-charged methamidophos and Cu^{2+}; (b) a complex action happened as methamidophos' amide ($-NH_2$) provided the free electron pair to Cu^{2+}, with the result that a part of the Cu^{2+} exited in soil solution in the form of soluble Cu^{2+} complex compound; (c) some new chemical

Table 2. Correlation coefficients （r） and standard errors （S_e） of four kinetics equations for Cu^{2+} sorption by soils （25℃）

Soils	Methamidophos concentration (mg L^{-1})	Elovich equation $Y=A+B\ln t$		Parabolic diffustion equation $Y/Y_{max}=A+B\sqrt{t}$		Two-constant equation $\ln Y=A+B\ln t$		First-order equation $\ln(Y_{max}-Y)=A+B\ln t$	
		r	S_e	r	S_e	r	S_e	r	S_e
Phaeozem	0	0.9146***	0.1869	0.9323***	0.0131	0.9155***	0.0155	-0.8695**	0.2723
	600	0.9034***	0.4667	0.7736**	0.0494	0.9064***	0.0374	-0.6570*	0.8563
	1200	0.9557***	0.3036	0.8055**	0.0446	0.9492***	0.0263	-0.8767***	0.8060
Burozem	0	0.9618***	0.8336	0.8415**	0.0427	0.9592***	0.0253	-0.9064***	0.3398
	600	0.9692***	0.7967	0.8890***	0.0368	0.9678***	0.0227	-0.8850***	0.5239
	1200	0.9725***	0.9738	0.8390**	0.0543	0.9633***	0.0311	-0.9403***	0.5063

Table 3. Correlation coefficients （r） and standard errors （S_e） of four kinetics equations for Cu^{2+} desorption by soils （25℃）

Soils	Methamidophos concentration (mg L^{-1})	Elovich equation $Y=A+B\ln t$		Parabolic diffusion equation $Y/Y_{max}=A+B\sqrt{t}$		Two-constant equation $\ln Y=A+B\ln t$		First-order equation $\ln(Y_{max}-Y)=A+B\ln t$	
		r	S_e	r	S_e	r	S_e	r	S_e
Phaeozem	0	0.8937***	3.0045	0.7112*	0.0030	0.8929***	0.0019	-0.9485***	0.3331
	600	0.9277***	12.4433	0.7456*	0.0143	0.9250***	0.0084	-0.9908***	0.1301
	1200	0.8938***	18.2381	0.6921*	0.0190	0.8894***	0.0125	-0.9810***	0.2535
Burozem	0	0.9490***	4.5803	0.8020**	0.0055	0.9482***	0.0030	-0.9574***	0.1913
	600	0.9885***	8.3163	0.8823***	0.0182	0.9867***	0.0067	-0.9708***	0.1846
	1200	0.9773***	11.9279	0.8452**	0.0216	0.9735***	0.0098	-0.9860***	0.1443

Y is the Cu sorbed (mg kg^{-1}), t is the time (min), A and B are model constants, r is correlation coefficients, S_e is standard errors, and the bigger is r, the smaller is S_e, the more perfect is the model, ***, **, * is significance at 0.001, 0.01, 0.05 levels, respectively.

compounds containing chelate group maybe produced as a result of some kind of uncertain chemical reaction between methamidophos and soluble organic matter in the soil solution, a part of Cu^{2+} exited in soil solution, in the form of soluble Cu^{2+} chelate, as the chelation reaction took place between Cu^{2+} and these chemical compounds. In a word, further studies are necessary to understand the chemical reaction which occurred between Cu^{2+} and methamidophos in the soil solution.

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