



## Effect of copper on the degradation of pesticides cypermethrin and cyhalothrin

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### Abstract

The influence of coexisting copper (Cu) ion on the degradation of pesticides pyrethroid cypermethrin and cyhalothrin in soil and photodegradation in water system were studied. Serial concentrations of the pesticides with the addition of copper ion were spiked in the soil and incubated for a regular period of time, the analysis of the extracts from the soil was carried out using gas chromatography (GC). The photodegradation of pyrethroids in water system was conducted under UV irradiation. The effect of Cu<sup>2+</sup> on the pesticides degradation was measured with half life ( $t_{0.5}$ ) of degradation. It was found that a negative correlation between the degradation of the pyrethroid pesticides in soil and Cu addition was observed. But Cu<sup>2+</sup> could accelerate photodegradation of the pyrethroids in water. The  $t_{0.5}$  for cyhalothrin extended from 6.7 to 6.8 d while for cypermethrin extended from 8.1 to 10.9 d with the presence of copper ion in soil. As for photodegradation,  $t_{0.5}$  for cyhalothrin reduced from 173.3 to 115.5 min and for cypermethrin from 115.5 to 99.0 min. The results suggested that copper influenced the degradation of the pesticides in soil by affecting the activity of microorganisms. However, it had catalyst tendency for photodegradation in water system. The difference for the degradation efficiency of pyrethroid isomers in soil was also observed. Copper could obviously accelerate the degradation of some special isomers.

**Key words:** degradation; photodegradation; copper; cypermethrin; cyhalothrin

### Introduction

Soil and water are two complicated ecosystems, where chemicals are degraded through physical, chemical and biological processes. The transportation paths of chemicals in these systems are often times different, which add the complication to study the fates of pesticides in a micro-scale. Mainly, the accumulation and degradation of pesticides and their dispersion in the environment depend on the characteristics and overall function of the ecosystem. In recent years, the synthetic pyrethroid pesticides are of growing importance in both agricultural and domestic applications, because of their high insecticidal activity, low toxicity to mammalian cells (Chaaieri Oudou and Bruun Hansen, 2002). Pyrethroid cypermethrin (CPM) and cyhalothrin (CHT) are widely used chemicals in this pesticide family. In orchard, they were often applied successively, and could enter into soil and the runoff near agriculture field by dropping from leaves through rain washing. On the other hand, copper was the main component in Bordeaux mixture (a mixture of copper sulfate and lime), which has been used to control mildew

in orchard for more than a century. As a fact that many metals possess good catalysis ability, copper might affect the behavior of coexisting pesticides in the soil and water.

The interactions of organic compounds and metals in the environment were well studied recently (Gaw *et al.*, 2003; Kools *et al.*, 2005, Shen *et al.*, 2005). The fate of pyrethroids (Lutnicka, 1999; Yu *et al.*, 1997) in the environment was also investigated. However, there were few studies on the influence of copper on the fate of pyrethroids in the environment.

In order to facilitate the understanding of the potential interactions between the pyrethroids and copper as well as proposing an effective method to remediate pesticides contaminated environment, extensive studies were carried out in our laboratories. The influences of copper on the degradation of pyrethroid pesticides in two different systems were evaluated, according to the half life of pesticide degradation measured in the presence and absence of Cu ions. Additional experiments were also carried out to investigate the difference of pyrethroid isomers degradation with/without copper.

## 1 Materials and methods

### 1.1 Materials and experimental conditions

The soil, collected near Dashahe orchard, Jiangsu Province, China. The soil at the surface layer (down to

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a depth of 15 cm) was taken and air-dried in laboratory. After mashed into fine particles it was passed through a 2-mm sieve. Its physico-chemical properties are shown in Table 1.

**Table 1 Properties of the soil studied**

Soil	OM (%)	CEC (cmol/kg)	pH (soil: H <sub>2</sub> O, 1:1, w/v)	Total Cu (mg/kg)
Sandy	1.04	6.18	8.26	76.0

OM: Organic matter; CEC: cation exchange capacity.

Two pyrethroid pesticides, i.e., cypermethrin (CPM, (RS)- $\alpha$ -cyano-3-phenoxybenzyl (1RS, 3RS; 1RS, 3SR)-3-(2,2-dichlorovinyl)-2,2-dimethyl-cyclopropane-carboxylate) (92.0%) and cyhalothrin (CHT, (S/R)- $\alpha$ -cyano-3-phenoxybenzyl (Z)-(1R/S, 3R/S)-3-(2-chloro-3,3,3-trifluoro-propenyl)-2,2-dimethylcyclo-propane-carboxylate) (95.2%) supplied by Redsun Co. Ltd., China were used. The chemical structures of the pyrethroids are illustrated in Fig.1 and their elementary properties are listed in Table 2.

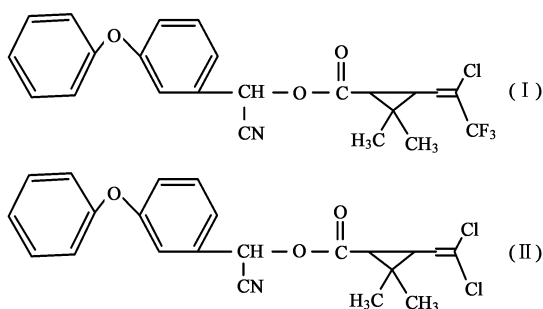


Fig. 1 Structure of cyhalothrin (CHT) (I) and cypermethrin (CPM) (II).

**Table 2 Elementary properties of the studied pyrethroids<sup>a</sup>**

Parameter	Cyhalothrin (CHT)	Cypermethrin (CPM)
CAS No.	91465-08-6	52315-07-8
Molecular weight	449.9	416.3
Number of isomers	2	8
Solubility in water (mg/L)	0.0008 (25°C)	0.004 (20°C)
$K_{ow}$ (L/kg)	$10^7$ (20°C)	$10^{6.6}$ (25°C)

<sup>a</sup> The data quoted from Chaaieri Oudou and Bruun Hansen (2002).  $K_{ow}$ : octanol/water partition coefficient.

Stock solutions of pesticides were prepared in menthol and kept in the dark at 4°C until use. Soil slurries were prepared by mixing 20.0 g of soil (dry weight) with 5 ml of water in 150 ml bottles, and then spiked with appropriate concentration of pyrethroid with Cu<sup>2+</sup>. The final concentration of Cu in soil was set as 10.0 mg/kg. The mixture was then incubated under controlled temperature for different experimental times. The control experiments without addition of Cu were also carried out. Immediately after the addition of the above substances the slurry bottles were sealed with cotton plug. After incubation for 0, 3, 7, 12, 20, 30 and 40 d respectively, the pesticides residue was analyzed by extracting from the incubated soil.

For photo-degradation experiment, the working solutions of perythroids at 2 mg/L and 4 mg/L with/without

addition of Cu<sup>2+</sup> were employed. The final concentration of Cu<sup>2+</sup> was 60 mg/L. The samples were irradiated by high pressure mercury lamp (220 × 3.25 W,  $\lambda \geq 365$  nm, Shanghai YaMin Lamp Co. Ltd., Shanghai, China) at intervals of 0, 10, 30, 60, 90 and 120 min. The resulting solutions were extracted for further GC analysis.

The analytical grade CuSO<sub>4</sub>·5H<sub>2</sub>O was purchased from Shanghai Tingxin Chemical Supplies (Shanghai, China). Organic solvents menthol and acetic ester used were chromatographic grade (Tedia Company Inc., OH, USA).

## 1.2 Quantitative analysis

Soil and water samples were ultrasonically extracted with 30 ml of acetic ester twice. The extracts of soil were filtered through 0.45  $\mu$ m polyethersulfone (PES) syringe filter membrane (Membrane Corporation, Germany). Additional 2 ml of acetic ester was passed through the syringe filter memberane twice. The extracts were then combined and dried with anhydrous sodium sulfate, evaporated to 5 ml by using a rotary evaporator and concentrated under a gentle stream of nitrogen at ambient temperature to a final volume of 1 ml. The concentrated extracts were stored at 4°C in glass vials for later analysis by gas chromatography. The extraction recovery was 65%–80% for soil samples and 85%–97% for water samples.

An Agilent 6890 gas chromatography equipped with an electron capture detector (GC-ECD) was used for the detection of pyrethroids. DB-5 silica capillary column separation of the pyrethroids was obtained using the following oven temperature program: 100°C, hold 1 min; 50°C/min to 260°C, hold 1 min; 5°C/min to 280°C, hold 35 min. Temperatures of injectors was 250°C and detectors was 300°C.

The half life of degradation for the pesticides was calculated by equation:

$$\ln C = -Kt + \ln C_0 \quad (1)$$

where,  $C$  is the concentration of extracts,  $C_0$  is the initial concentration of test compounds,  $t$  is the degradation time and  $K$  is the degradation rate.

The tests were carried out in three replicates and the data expressed average effect of the test points.

## 2 Results and discussion

### 2.1 Degradation in soil

Figure 2 demonstrates the degradation trends of CHT and CPM in the soil. The degradation curves can be divided into two distinct stages: active and lag-phase degradation. CHT degraded quickly at the beginning of the tests and then slowed down after 12 d, while for CPM the rate of the degradation reduced after 20 d. The calculated half-life for CHT was 6.7 d. When copper was present, it increased to 6.8 d. This might suggest that the presence of copper in the soil inhibited the degradation of CHT. As for CPM, the half life ( $t_{0.5}$ ) varied from 8.1 to 10.9 d under the same conditions as of CHT.

The degradation rate of an organic chemical in the soil

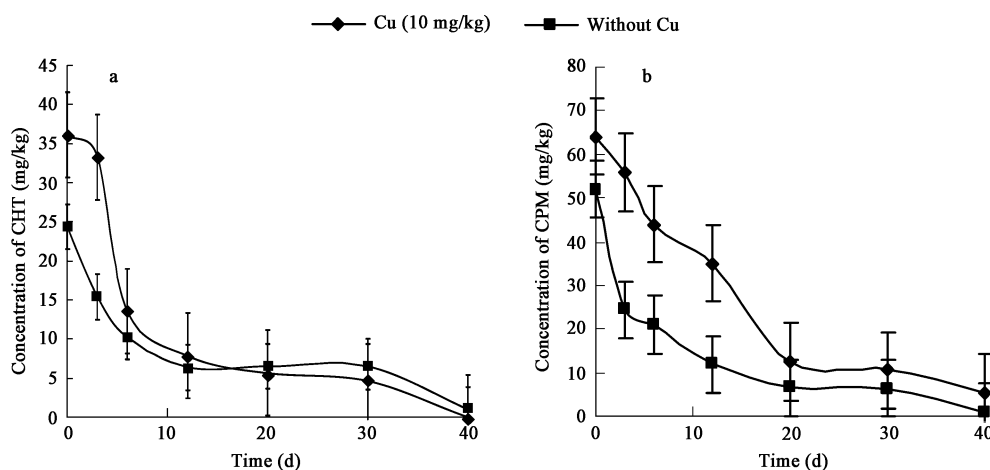


Fig. 2 Degradation profiles of the pyrethroid in soil. (a) CHT:  $\ln C = 3.60 - 0.103t$ ,  $r = -0.85$ ,  $P = 0.0096$ ,  $SD = 0.3911$  for CK;  $\ln C = 3.29 - 0.102t$ ,  $r = -0.94$ ,  $P = 0.0468$ ,  $SD = 0.359$  for tests with Cu(II) (10 mg/L); (b) CPM:  $\lg C = 3.63 - 0.081t$ ,  $r = -0.96$ ,  $P = 0.0033$ ,  $SD = 0.3842$  for CK;  $\ln C = 4.16 - 0.0638t$ ,  $r = -0.984$ ,  $P = 5.715 \times 10^{-4}$ ,  $SD = 0.206$  for tests with Cu (10 mg/L), SD is standard deviation for the fit.

is closely related to its availability to enzymatic systems of microorganisms. The nature and extent of the retention of organic compound depended not only on its intrinsic properties (Lutnicka *et al.*, 1999), but also on the properties of the soil, which was mainly represented by the amount and nature of organic matter (Sa'nchez *et al.*, 2004). In our experiments, the molecule of CHT, differing from CPM only by a halogen group, degraded more efficiently.

Under the same experimental conditions, different degradation rates resulted from different chemical structures triggered our interest in studying the degradation differences of isomers. CPM isomers are studied with/without the addition of copper ion. The chromatograms of the CPM isomers standards are shown in Fig.3a. Fig.3b shows the residues of different CPM isomers in soil after incubation. From these chromatograms, the preliminary results shown that the ratio of the CPM isomers has slight change after a 3-d incubation with Cu addition, while in the control experiment that without Cu addition, the isomers 1, 3 and 4 reduced more than 50%, but isomer 2 still showed the similar amount in the soil after being incubated for 3 d. The degradation difference of isomers might be due to the selective degradation by soil microorganisms occurring at special environment (Ma *et al.*, 2005). The ability of

microorganism communities to degrade xenobiotic compounds was highly soil-specific and degradation selection varied in different soils.

Generally, it was believed that heavy metals influenced the degradation of pesticides by affecting the activity of soil microorganisms. Kools *et al.* (2005) have reported a positive correlation between glyphosate degradation rates and soil metal pollution. Contrary to their research, the inhibition of pyrethroid degradation caused by copper ion was observed in this study. According to Ellis *et al.* (2001), copper, zinc concentrations and pH showed significant correlation with the microbial parameters. The enzymatic reactions were inhibited by metals which may complex with the substrate, combine with the protein-active groups of the enzymes, or react with the enzyme-substrate complex. That metal reacting with sulfhydryl group led to inactivation or inhibition of enzyme activity. Thus bacterial biomass activity might be inhibited in copper polluted soil. The inhibition of pyrethroid degradation could be explained as copper effect on bacterial biomass activity, although it is not clear about the exact mechanisms by which copper interacts with enzymes in soils.

Further experiments are needed to study the possible inhibition of copper to the degradation pathways of mi-

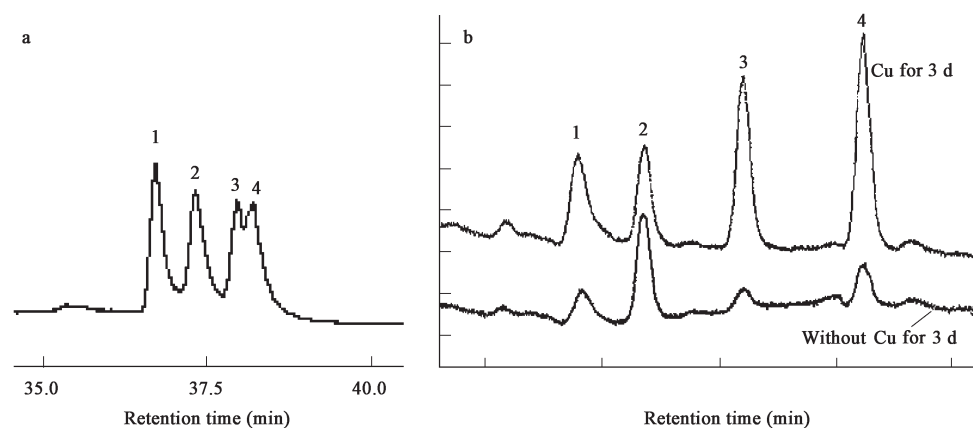


Fig. 3 Chromatograms of CPM isomers. (a) gas chromatograms for the CPM isomers; (b) the effect of Cu on the degradation of CPM isomers. Peaks 1, 2, 3, 4 represent isomers of CPM.

**Table 3** Effect of Cu<sup>2+</sup> on photodegradation of pyrethroids in aqueous solutions

Pyrethroid	Cu (mg/L)	$\ln C = -Kt + \ln C_0$	$t_{0.5}(\text{min}) = \frac{0.693}{K}$	<i>P</i>	SD
CHT	0	$\ln C = -1.1 - 0.004t, r = -0.95$	173.3	0.012	0.073
	10	$\ln C = -0.97 - 0.006t, r = -0.95$	115.5	0.014	0.095
CPM	0	$\ln C = -0.61 - 0.006t, r = -0.95$	115.5	0.013	0.105
	10	$\ln C = -0.086 - 0.007t, r = -0.98$	99.0	0.003	0.074

croorganism and understand its affects on the regulation system.

## 2.2 Photo-degradation in water

The degradation of pyrethroids in soils was investigated. The main factor was hypothesized as the inhibition of copper to the enzymatic system of the microorganism. However, in the environment, pyrethroids usually degrade through photolysis, photo-oxidant and photo-isomerization (Bi *et al.*, 1996). As there are unstable groups such as isobutyl- and double bond in the structure of pyrethroids, photolysis is possibly the main degradation path of pyrethroids in the environment. In the degradation process of pyrethroids, the influence of coexisting heavy metal cannot be ignored as some heavy metal has catalysis ability. To have a better understanding of the different functional mechanism of degradations, the photodegradation experiments were carried out in pure water system to avoid the interference factors might be caused by microorganisms.

Copper and its coordination compounds may play the role of a catalyst for photodegradation of various pollutants in irradiated systems. This catalytic effect can be based in principle on the photodegradation of the pollutant as a ligand in the coordination sphere of the copper central atom and/or on the secondary thermal reactions of the active species produced photochemically from the copper complex (Sýkora, 1997). According to Sýkora, there was a Cu(II)-Cu(I) photo catalytic redox cycle in copper solution.

Table 3 shows the photo-degradation parameters of CHT and CPM. The degradation rates were increased after Cu(II) addition into the photo irradiation system.  $t_{0.5}$  varied from 173.3 min to 115.5 min for CHT and 115.5 min to 99.0 min for CPM. This indicated quick degradation of tested pyrethroid under UV light which was accelerated by copper. It could be deduced that in natural environment, the residual life of selected pyrethroids were relatively short mainly due to the influences of the coexisted compound on its degradation behavior.

Therefore, with the presence of Cu(II), CPM and CHT degraded quickly under the irradiation of UV light. It can be deduced that in the water, the pyrethroids could disappear at a short time in the event of enough sunlight exposure and the existence of some heavy metals such as copper. This result may be extrapolate to soil solution, because there are the same environmental factors such as water in the two different systems.

Mařtovská and Lehotay (2004) had reported that the  $\alpha$ -cyano substituted pyrethroids could convert to their diastereoisomers either by isomerization (racemization) at the  $\alpha$ -position or by *cis*-/*trans*- isomerization (recombi-

nation on the cyclopropane ring), which was the main photodegradation pathway for deltamethrin exposed to ultraviolet or sunlight irradiation. However in this study, isomers conversion had not been observed, which maybe the ratio is too fast to catch any intermediates.

## 3 Conclusions

Soil degradation and photodegradation of CPM and CHT were affected by coexisting Cu(II). The added copper could catalyze photodegradation of CPM and CHT in aqueous solution while its degradation inhibition in soil was observed. Isomers degradation variation for the pyrethroids in the soil was also observed, Cu facilitated some isomers degradation.

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