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Review the environmental behaviour of insecticide 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea

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Abstract The environmental behaviour of insecticide 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea (CCU) were studied. The results indicated that the insecticide concerning the risk assessment and safe for application of the chemical was not a long-persistent compound in the environment and degraded fastly in plant, soil, water and air. The major degradation products of CCU were found to be 4-chloroaniline, 4-chlorophenyl urea, 2-chlorobenzamide, 2-chlorobenzoic acid, chloroisocyanatobenzene and 2-chloro-N-chlorophenyl benzamide. The study demonstrated that the insecticide would not be harmful to environment, especially to groundwater. However, attention should be paid to the potential problem caused by its degradation products.

Keywords: pesticide; 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea; bioaccumulation.

INTRODUCTION

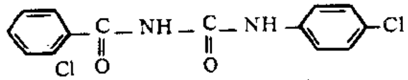
The insect growth regulator 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea (CCU) was devoloped in China starting from 1976, and it has been widely used for the control of such destructive insects as pine moth of forestry, armyworm of wheat and corn, cabbage caterpillar of vegetable in China (Chen, 1980; 1981; 1984; Lu, 1981). CCU was proved to be a compound of low toxicity as its acute oral LD_{50} for rats and for mice are greater than 10000 mg/kg, it is not toxic to birds, fishes and bees, and exerts no effects of teratogenesis and mutagenesis (Sun, 1982; Lu, 1983).

Systematic studies on residue and degradation of CCU in plant, water, soil, air and fish were reported laterly (An, 1990; Zhou, 1992; Jobelius, 1990; Xu, 1990; Yang, 1990; 1991; 1992; Shi, 1992; Liu, 1992; Yang, 1992; Mo, 1991; 1992; Zhang, 1992). Most of the studies are presented in this issue. In this paper, some of the studies on the environmental behavior of CCU related to its risk assessment and safe use of the pesticide were reviewed and discussed.

ENVIRONMENTAL BEHAVIOR OF CCU

1. Physical and chemical properties of CCU

The structural formula of 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea (CCU), $C_{14}H_{10}Cl_2N_2O_2$, is as follows:



MW = 309.16

The pure compound of CCU is a colourless crystal with melting point of 199 – 200°C and a water solubility of 0.17 ppm (25°C). Its n-octanol/water partition coefficient (log K_{ow}) is 3.57. The organic carbon sorption constant of the compound in soil (K_{oc}) is about 1600. Its saturated pressure at 25°C is 2.05×10^{-4}Pa, and Henry's constant (H) is 1.6×10^{-4} (Yang, 1991). The bioconcentration factor (BCF) of CCU is 17 – 75 (Jobelius, 1990; Zhang, 1992).

2. Residue and persistence of CCU in soil and vegetables

The insecticide CCU is not a long-persistent compound, as it is unstable in environment. Field studies on residue and persistence of CCU in Chinese cabbage and soil were carried out in both the northern and southern China during 1988 – 1989. Experimental results showed that CCU possesses a half-life of 3.8 – 14.0 days in Chinese cabbage, and a half-life of 8.8 – 27.0 days in soil, respectively. It means that CCU in Chinese cabbage disappears more rapidly in the southern China than in the north. The maximum residues of CCU in Chinese cabbage were 0.83 and 11.87 ppm on the 7th day, 0.43 and 3.28 ppm on the 14th day, 0.16 and 2.67 ppm on the 21th day and 0.04 and 1.78ppm on the 28th day after the last application at rate of 150 or 300 g a.i./ha and with application frequencies of 2 or 3 times in the northern and southern China, respectively. Meanwhile, the maximum residues of CCU in soil were 0.01 and 30.01 ppm on the 7th day, 0.09 and 18.56ppm on the 14th day, 0.05 and 13.81ppm on the 21th day in the northern and southern China, respectively. It seems that CCU persists for a longer time in acidic soil in southern China than in basic soil in the north.

3. Degradation of CCU

(1)Degradation of CCU by soil microorganisms

Owing to the effect of microorganisms in soil, insecticide CCU disappears more rapidly in the field. Some microorganisms in soil that could degradate CCU were separated in the laboratory (Shi, 1992). These are ps. *alcaligenes*, *acinetobacter calcoacticus*, ps. *testoeteroni*, *brevibacteriam* sp., *cladosporium* sp., *penicillium* sp., *aspergillus* sp. and *trichoderma* sp. The concentration of CCU in soil could be reduced by 26 – 97% after being incubated for 5 days with different microorganism at 25°C. The half-life values of CCU were 1.3 – 3.5 days when incubated with different microorganisms at 28°C. The main metabolites of CCU were 4-chlorophenyl urea, 4-chloroaniline, 2-chlorobenzamide and 2-chlorobenzoic acid. The following degradation pathway of CCU is suggested (Fig. 1).

(2)Hydrolysis of CCU

Hydrolysis experiments of CCU in buffer solution show that the compound is unstable in water. The half-life values of CCU in buffer solution at pH 5, 6, 7, 8, 9 and 10 (25°C) are 35.5, 8.8, 5.7, 4.7, 3.5 and 1.9 days, respectively. The hydrolysis rate of CCU increases with increasing pH and media temperature. The temperature coefficient for hydrolysis reaction of CCU is 2.5 and the activation energy (E) for the reaction is 71.56 kJ/mol. Major products of CCU are 4-chlorophenyl urea, 4-chloroaniline, 2-chlorobenzamide, 2-chlorobenzoic acid and 4-chloroisocyanatobenzene and the pathway for CCU hydrolysis is suggested below (Fig. 2).

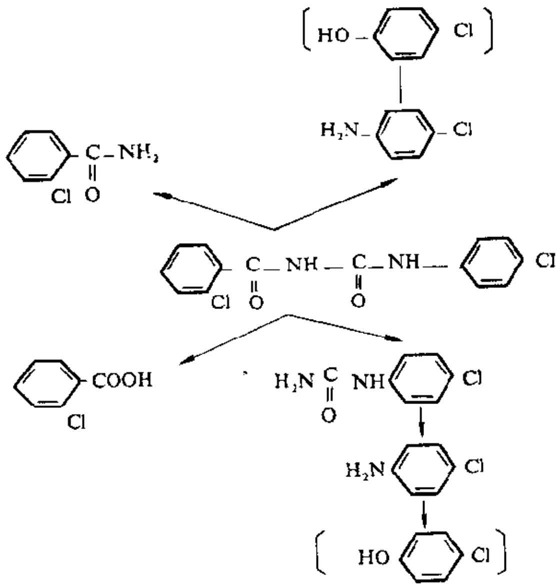


Fig. 1 Microdegradation pathway of CCU

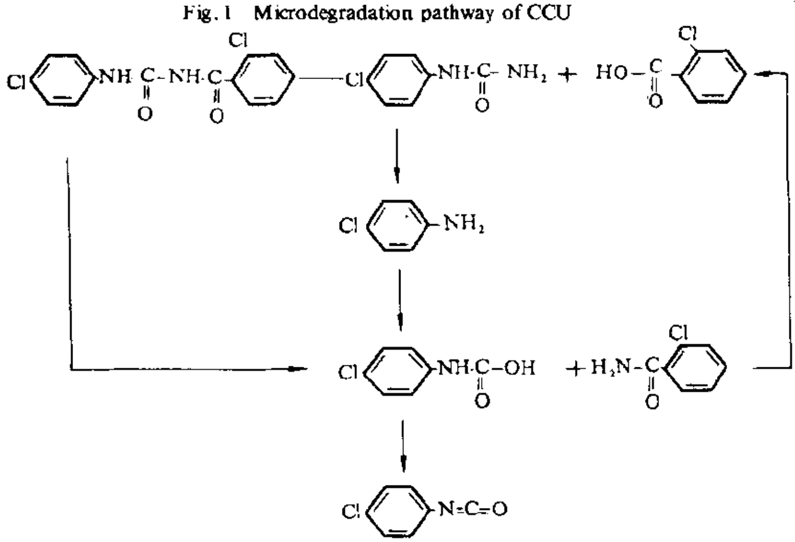


Fig. 2 The pathway for the hydrolysis of CCU

(3) Photodecomposition of CCU

It is found that CCU is unstable to UV radiation. The photoreaction of CCU in nitrogen and air fit the first order reaction kinetics, while in oxygen the photodegradation of CCU could approximately described by a second order reaction kinetics. The half-lives for the photodecom-photodecomposition of CCU in nitrogen, air and oxygen are 4.11, 2.65 and 2.61 days, respectively. The main photoproducts of CCU are 4-chlorophenyl urea, 4-chloroaniline, 2-chlorobenmide and 2-chloro-N-chlorophenyl benzamide. CCU also degradates and reacts with methanol under UV radiation. The photodecomposition pathway of CCU is suggested in Fig. 3 (Liu, 1990).

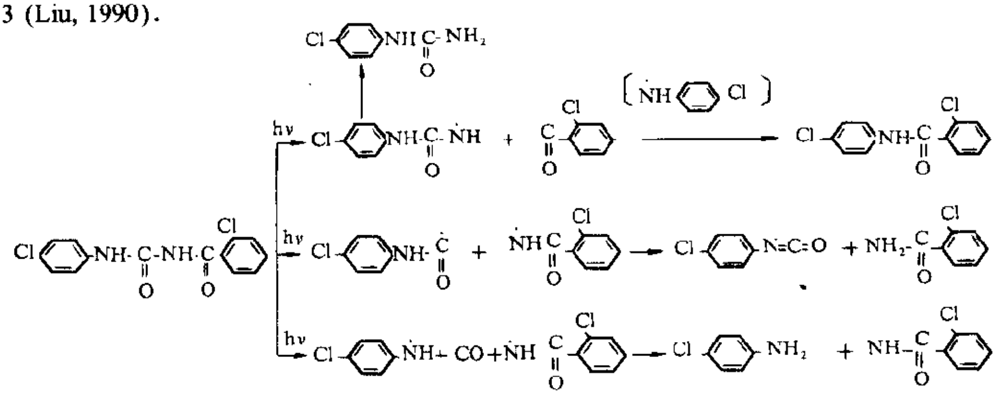


Fig. 3 The photodecomposition pathway of CCU

4. Bioaccumulation of CCU

According to the values of water solubility (0.17ppm) and n-octanol/water partition coefficient (log $K_{ow}=3.57$) (Yang, 1990), CCU should possesses a medium capability of bioaccumulation. However, Zhang reported that CCU possesses a bioaccumulation of comparatively low (< 100) measured bioconcentration factor in fish (BCF, Zhang, 1992). It has also been reported that CCU could be degradated quite rapidly by enzymes like esterase in fish, implicating that CCU would not harmful effect to human through food chain.

5. Movement of CCU

As a nonpolar compound with a water solubility of 0.17 ppm, CCU was found to be comparatively strongly adsorbed by soil particles with a K_{oc} value of 1600. This suggested that CCU would possess a low mobility in soil.

The experimental results of CCU in soil column of 21 cm in length and 3.46 cm in i.d. showed that when the total precipitation was 200 mm and duration of the tests was 24 hours, CCU moved slowly in loam soil, sandy loam soil and sandy soil, 95% of CCU residues remained in the soil column were in the 0–3 cm upper layer of soil column. The maximum leaching depth of CCU in soil column was only 4.5cm.

Results of another leaching experiment of CCU in sandy loam soil in plexiglass column of 80 cm in length and 10.54 cm in i.d. represented the active process of CCU leaching in soil. When the precipitation was 173, 183 and 186 mm for A, B and C column and the leaching time was 29.5, 33.5 and 34.7 hours, respectively, the maximum leaching distance of CCU in soil was

12.5 cm with residue levels equal to 0.01 or 0.02 ppm. This suggests that it is unlikely that CCU would reach groundwater through leaching in the area where the insecticide was applied.

Based on the results obtained with soil columns under laboratory conditions, a model which describes the transport and transformation of pesticide in unsaturated soil was developed and used to predict CCU pollution tendency of groundwater (Yang, 1992). The model is simple and effective for prediction, however, it needs to be further developed to assess pesticide leaching behavior in the field.

CONCLUSIONS

The insecticide CCU is unstable in plants, soil, water and to UV radiation. As it possesses a low water solubility, it could be comparatively strongly adsorbed by soil particles and hence moves slowly in soil. The compound has a low bioconcentration capability. CCU is not volatile as well. Thus, the insecticide would not cause remarkable environmental pollution problem.

Two or three times applications with a dosage of 150 g a.i./acre and safe time interval of days are recommended for agricultural practice. The MRL value of 3 ppm of Chinese cabbage is suggested. However, the residues of CCU in soils, especially in the southern China, should be observed with close attention.

The major degradation products of CCU are 4-chloroaniline, 4-chlorophenyl urea, 2-chlorobenzamide, 2-chlorobenzoic acid, 4-chloroisocyanatobenzene and 2-chloro-N-chlorophenyl benzamide. It should be noticed that among the breakdown products, 4-chloroaniline, 4-chlorophenyl urea are potentially harmful, and 2-chlorobenzamide might be genotoxic. Therefore, attention should be paid to the potential problems of some of the degradation products of CCU.

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