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Study on the residue of 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea in Chinese cabbage and soil in the Southern China and its distribution in laboratorial microcosm

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Abstract. This paper discusses the residue of 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea (CCU) in Chinese cabbage and soil in the Southern China. Under single factor controlled condition, the distribution and transformation of CCU in microcosm are described.

In field trial of two consecutive years, the results show that the half-life values of CCU in Chinese cabbage and soil in the Southern China are 3.8–4.1 days and 10.9–11.6 days; respectively. The experimental results in laboratorial microcosm demonstrate the fortnight half-life of CCU in soil. Vegetables lack of enough ability to absorb CCU from soil and accumulate on roots. Although there are a certain amount residues of CCU in soil, it is impossible to bring about serious pollution after routine application is carried out.

Keywords: pesticide; 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea; residues; Chinese cabbage; microcosm.

INTRODUCTION

1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea (CCU) is a new insect growth regulator (IGR), developed first by Jiangsu Normal University (Cheng, 1979) in China in the seventies. There are many reports on 1-(4-chlorophenyl)-3-(2, 6-difluorobenzoyl) urea, and 1-(4-chlorophenyl)-3-(2, 6-dichlorobenzoyl) urea abroad (Corley, 1974; Lawrence, 1976; Worobey, 1977; Dehler, 1975). However, the information relating to CCU is scarce.

This paper reports field trial results of the residue and persistence of CCU in vegetable and soil in Shanghai during 1988–1989. Besides these, the investigation of its distribution and

transformation in model vegetable-soil system are also reported.

EXPERIMENT SECTION

In field trial

1. Analytical method

The samples of Chinese cabbage and soil after being extracted with CH_2Cl_2 were analyzed by high performance reverse-phase liquid chromatography. Cabbage samples must be purified by passing through pre-wetted silica gel column before analysis.

2. Experimental method

Field trials were performed in Congming County of Shanghai during 1988－1989. According to routine spray method in which 150 or 300 g CCU a. i. /ha was applied for each spray, Chinese cabbage were sprayed twice or three times with 25% CCU suspending gel diluted to 2500 times with water. The amount and frequency of spray are shown in Table 1.

Table 1 The design of trial field*

Serial of trial field	Experimental area, m^2	Amount of CCU, g a. i./ha	Frequency of spray	Interval between sprays, days
1	30×2	150	2	10
2	30×2	150	3	15
3	30×2	300	1	—
4	30×2	300	2	10
5	30×2	300	3	15
6	30	0	0	—

* Date of experiment: Sep. － Dec., 1988; 1989.

In microcosm

1. Transplantation experiment of vegetable

A desiccator (300 mm in diameter, volume 10 liters) was used for plant growing. Vegetable was transplanted into 2 kg of soil (1400 g vegetable field soils mixed with 600 g sand, pH-value was 6.4, organic carbon content was 3.14%) treated with 25% CCU suspending gel solvent (at a initial concentration of 50.09 ppm). 9 days after planting, soil and vegetable samples were collected. In another similar desiccator, disappearance experiment of CCU in soil was carried out from first day.

2. Cultural experiment of vegetable seeds

Three kilogram soil (the same as prior condition) were loaded into another similar installation with 467.8 mg of CCU standard materials applied. This concentration of CCU was about 156 ppm in soil. Green vegetable seeds were sown in it and soil moisture capacity was kept up

to 13%. Having been sown for 56 days, vegetable seeds sprout and grow up. Collected soil and vegetables at appropriate amount for preparing samples.

3. Preparation of sample

Vegetable samples were separated into roots and leaves after gathering. Homogenized with adding CH_2Cl_2 for extraction, cleaned up by chromatographic column packed with pre-wetted silica gel. Evaporated using K. D. evaporator to near dryness and to the marked volume with adding methanol. Stired soil samples uniformly after sampling and divided them into two 50 g aliquots and determined moisture content of one soil sample. Saturated another part with CH_2Cl_2 for 15 h, added appropriate amount of anhydrous Na_2SO_4, homogenized it in high speed blender for half a minute. Successively filtered CH_2Cl_2 extracts on Buchner funnel with suction pump, and then washed with 3×50 ml CH_2Cl_2. Merged filtrate to concentrate in K. D. evaporator and mark volume with methanol to 0.5 ml as soil sample (*a*). Homogenized the surplusage of soil for 30 seconds, extracted by methanol again, filtered and washed using 50 ml$\times$3 methanol solvent. Combined all the extraction solution to evaporate to 0.5 ml volume as soil sample (*b*).

4. Operating apparatus and condition of high performance liquid chromatography

The HPLC was carried out via Shimadzo LC 5A type equipped with SPD-2AM-UV detector, the monitor wavelength was selected at 254 nm, chromatographic column used was 150mm$\times$4.6 mm I.D. with filled Zorbax C_8 packing, mobile phase was a mixture of methanol-water (8: 2), flow rate was 0.3 ml/min; sensitivity was 0.01 AUFS, retention time of CCU ranges was 9.0$-$9.4 minutes. The detected limit is 10 ng, the lowest detection limit concentration of detectibility for the green vegetables and Chinese cabbage is 0.05 ppm and the average recovery for vegetable samples is 95.1%.

RESULTS AND DISCUSSION

1. Persistence of CCU in vegetable and soil

The CCU residue degradated rapidly in the first week with an average degradation rate of 75% (Table 2). After 15 days, the concentration of CCU became very low and the degradation slowed down. After 20 days, 95% of CCU has been degradated. The trends of degradation are also shown in Fig. 1.

The trend of degradation is described in the following equation:

$$1988: C=19.87e^{-0.1697t} \qquad r=-0.96 \quad T_{1/2}=4.1d;$$

$$1988: C=54.59e^{-0.1845t} \qquad r=-0.98 \quad T_{1/2}=3.8d.$$

The residue in soil (pH=6.40; organic compound: 3.14%) degradated rapidly at the first 10 days and then slowed down. It became constant after 90 days, with a degradation rate of more than 90% of the original amount (Table 3). The trend of degradation is shown in Fig. 2 and

Table 2 The degradation of CCU in Chinese cabbage

Unit: ppm

	Days after spraying								
	0	1	3	6	9	15	22	29	37
1988	31.87	22.78	12.30	5.10	3.17	0.49	0.41	0.24	ND*
1989	62.25	–	34.62	15.98	12.38	2.46	1.02	0.30	ND*

* ND < 0.05 ppm

is described in following equation:

1988: $C=2.23e^{-0.0598t}$ $r=-0.98$ $T_{1/2}=11.6$ d;

1989: $C=16.88e^{-0.0634t}$ $r=-0.98$ $T_{1/2}=10.9$ d;

As shown above, the half-life of CCU in Chinese cabbage and soil in the Southern China is 3.8–4.1 days and 10.9–11.6 days, respectively.

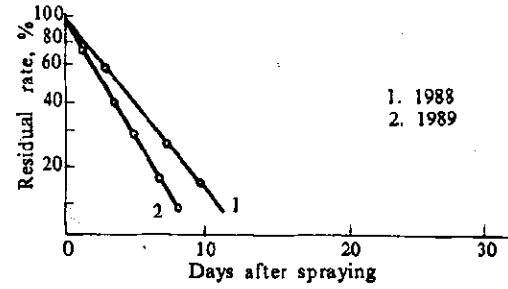

Fig. 1 The curve of degradation of CCU in Chinese cabbage

Table 3 The trend of degradation of CCU in soil

Unit: ppm

	Days after spraying											
	0	1	5	7	9	16	21	37	44	56	71	90
1988	2.57	2.12	1.45	1.39	1.30	0.81	0.61	0.49	0.49	–	0.3	0.26
1989	15.31	–	–	12.77	9.35	–	4.26	–	–	3.48		1.62

2. The residue of CCU in cabbage and soil

In two consecutive years, after routine spraying, Chinese cabbage was analyzed periodically (Table 4).

The results of six experimental in two years show that there is not relationship between the trend of degradation of CCU in cabbages and original amount of CCU.

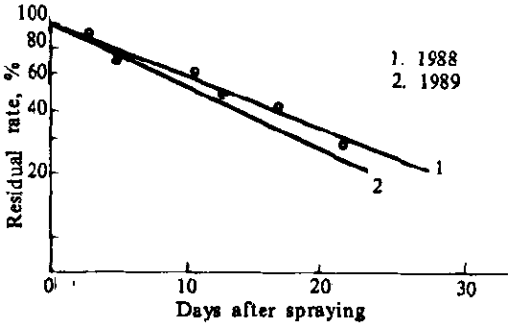

Fig. 2 The curve of degradation of CCU in soil

At the end of first, second, and third week, the residues of CCU are 1.36–11.78 ppm; 0.49–3.28 ppm and 0.20–2.67 ppm, respectively. According to the standard residue of 3 ppm CCU for wheat, it is recommended that the safety interval be 21 days after spraying 150–300 g a. i. /ha of CCU by 2–3 times.

Table 4 The residue of CCU in Chinese cabbage

Unit: ppm

Application dose of CCU, g/ha		Times	Days after spraying							
			0	7	14	21	28	35	42	49
1988	150	2	23.36	3.77	0.69	0.25	0.21	0.09	ND	
	300	3	4.26	1.36	0.49	0.38	0.24	0.22	0.18	ND
1989	150	3	21.70	2.44	2.76	0.20	ND			
	150	2	32.51	4.60	2.30	0.20	ND			
	300	3	47.50	7.25	2.25	2.67	1.78	0.20	ND	
	300	2	48.40	11.78	3.28	0.73	0.43	ND		

In parallel to the analysis of residue of CCU in cabbage, the residue of CCU in soil is also analyzed periodically. The experimental results are shown in Table 5.

Table 5 The residue of CCU in soil

Unit: ppm

Application dose of CCU, g/ha		Times	Days after spraying								
			0	7	14	21	35	49	63	83	90
1988	150	2	4.56	2.46	1.02	0.71	0.69	0.72	0.63		0.40
	300	3	4.87	2.46	1.62	–	1.31	–	1.21	–	1.11
1989	150	3	43.06	–	9.08	7.59	3.37	–	–	1.81	–
	300	3	42.75	18.95	13.51	11.61	7.65	–	3.44	–	–
	300	2	40.52	30.01	18.56	13.81	10.29	2.81	–	1.89	–

The results show that the maximal residue of soil is 13.89 ppm after three weeks and is 1.11 ppm after three months. Thus, the pollution of CCU in soil is a remarkable environmental problem.

3. Degradation trend of CCU in microcosm soil

In microcosm, degradation rate of CCU in soil is shown in Table 6. Apparently 50% amount of CCU applied degraded rapidly at the first 14 days, and then the degradated rate trends to the low level (about 80%) 36 days later. More than 90% CCU of original amount had degraded 70 days later (Fig. 3). It disappeared completely in a little over three months, although the half-life of CCU in soils was 14 days.

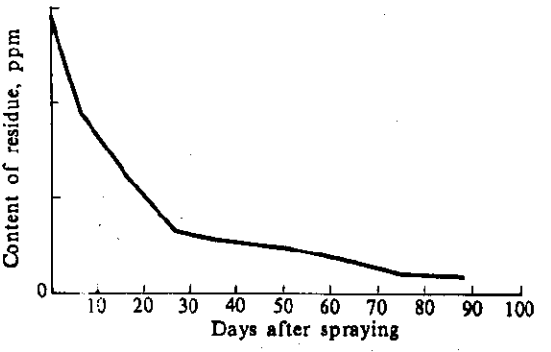

Fig. 3 The residual trend of CCU in soil

Table 6 The degradation trend of CCU (III) in model vegetable-soil ecosystem

Days after spraying	0	8	16	28	36	48
Residue of CCU in dry soil, ppm	56.80	37.59	25.79	12.68	11.39	10.48
Days after spraying	52	61	65	73	90	
Residue of CCU in dry soil, ppm	10.22	7.06	6.59	4.37	3.50	

4. Absorption and distribution of CCU in vegetable-soil ecosystem

Cultural experiment shows that after 9 days 2.31 ppm of CCU was found in green vegetables which is apparently absorbed from the soil containing initial 50 ppm of CCU. 79.82% of initial concentration was also found in the soil (Table 7). The residue absorbed by vegetable from soil is merely 0.014% of the total amount. In addition, the experimental results of sample (*a*) and sample (*b*) indicate that the recovery is as high as 98.33% by using CH_2Cl_2. So it is satisfactory to prepare soil samples by using CH_2Cl_2 only.

Results of seed cultural experiment are shown in Table 8.

The pesticides absorbed by green vegetable from the soil is 0.018% of the total amount according to weight equivalence, and is mainly accumulated in the root which is five times as much as in the leaf. 88.37% of residues in soil have been converted during field experiment. To sum up, the half-life of CCU in soil is 14 days, the period of degradation is over 3 months. The

Table 7 Distribution of CCU in vegetable-soil microcosm ecosystem 9 days after spraying

Sample	Value of CCU detected, ppm	Sample weight, g	Distribution, %
Green vegetable	2.31	6.0	0.014
Soil	(*a*) 39.31* (*b*) 6.68*	2000	79.8
Deviation			20.2

* Residue in dry soil, initial concentration of CCU is 50.09 ppm

Table 8 Distribution and weight equivalence of CCU in vegetable-soil microcosm ecosystem

Sample	CCU found, ppm	Sample weight, g	Total residue, mg	Weight equivalence
Green vegetable				
leaf	1.05	63.37	0.067	0.014
root	5.49	3.26	0.018	0.004
Soil	18.08	3600	54.24	11.61
Deviation				88.37

ability of vegetable absorbing CCU from the soil is insignificant and concentrate in roots mainly. The more amount of CCU is applied in the soil, the more residues occur in soils. There are hardly any high residues in vegetables with ordinary dosage spraying, although a certain amount of residues are found in the soil.

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