

STUDY ON RESIDUES OF ^{14}C -CARBOFURAN IN MODEL RICE-FISH ECOSYSTEM*

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ABSTRACT

Residues of ^{14}C - carbofuran were studied in model late- rice ecosystem (LRE) and early- rice ecosystem (ERE). The treatment consisted of two rates of the pesticide (1x and 2.5x). At day 56 after application, 7.3% (1x) and 2.9% (2.5x) of the pesticide and its degradative products remained in the water of the LRE, and 1.8% (1x) and 2.4% (2.5x) of them remained in the water of the ERE. At harvest, 37.5% (LRE) and 24.0% (ERE) of the pesticide applied were detected in the upper layer of the soil; and 40.6% (LRE) and 26.9% (ERE) remained in the lower layer of the soil. The residues in the rice plants increased at the first stage, reached maximum levels during day 14 to 28 after application, and decreased thereafter. At harvest, residues in the stems and leaves in the two treatments (1x and 2.5x) were 3.91 $\mu\text{g/g}$ and 7.78 $\mu\text{g/g}$ (LRE) and 5.04 $\mu\text{g/g}$ and 17.29 $\mu\text{g/g}$ (ERE) respectively. Residues in the ears were about 1/8 to 1/12 of that in the other parts of the plants. The pesticide residues in fish bodies in both experiments were also determined.

Keywords: Carbofuran Residue Model rice- fish ecosystem

I. INTRODUCTION

Carbofuran (2,3- dihydro- 2,2- dimethyl- 7- benzofuranyl- N- methyl carbamate) as an insecticide has been widely used in crop production. Its metabolism in cotton, maize, bean, etc. has been studied in detail. However, reports regarding its absorption, metabolism and retention in rice- fish ecosystem were scarcely published. The present study was designed based on the Recommendation of FAO/IAEA Consultant Meeting in 1983 to investigate the residues of ^{14}C - carbofuran in model rice- fish ecosystem. Both late rice (in 1986) and early rice (1987) have been tested.

II. MATERIALS AND METHODS

1) *Model chamber* Water- tight glass tanks with the size of 60× 40× 40 cm (in LRE) or 70× 60× 40 cm (in ERE) were used to keep water, soil, fish and rice plants and formed the model ecosystem. They were kept in a greenhouse with the same temperature, humidity, ventilation and lighting conditions as those in the neighbouring areas.

2) *Insecticide* ^{14}C - carbofuran (furanyl- 3- ^{14}C labeled), with the specific activity

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of $3.5783 \times 10^6 \text{Bq/mg}$ and radiochemical purity over 97%, was synthesized by the Institute of Isotopes of Hungarian Academy of Science. Unlabelled carbofuran granules (3%) were provided by Wuhan Agrochemicals Plant.

Two treatment levels, 1x, i.e. common dose and 2.5x, were used in the studies. In the case of LRE, 18 mg ai/tank with the activity of $3.119 \times 10^6 \text{Bq/tank}$ (1x) and 45 mg ai/tank with $7.7959 \times 10^6 \text{Bq/tank}$ (2.5x) were applied. In ERE, 32.7 mg ai/tank with activity of $5.9866 \times 10^6 \text{Bq/tank}$ (1x), and 81.6 mg ai/tank with $1.497 \times 10^7 \text{Bq/tank}$ (2.5x) were used. The insecticides were fully mixed with the soil.

3) *Soil* Paddy soil (organic matter: 2.95%; sand: 16.18%; clay: 26.42%; silt: 57.4%; pH 6.4) collected from Sichuan Agricultural University Farm was sieved through 10 mm mesh before use. 40 kg (LRE) or 60 kg (ERE) of the air-dried soil were filled in each tank in the depth of 15 cm.

4) *Water* After keeping for more than one week, 24 litres (LRE) or 32 litres (ERE) of tap water was filled in each tank. Water levels in the tank were adjusted as follow: At transplanting to a depth of 3 cm above the soil surface; after releasing the fish to a depth of 6 cm; and 30 days later to 10 cm.

5) *Rice plants* In LRE, the variety "Shu Feng No. 1" matured in 125 days was selected in the experiment. Four hills per tank and 3 seedlings per hill with the density of 20×30 cm were arranged. The variety "Lu Hong Zao" matured in 120 days was grown in ERE. Transplantation was made at the density of 20×15 cm, 9 hills each tank and 1 seedling per hill.

6) *Fish* Six common carps with 5.8 cm in length and 5.2 g in weight were released in each tank at day 5 after transplantation. No feed was given during the experiments.

7) *Sampling and measurement* Water: At day 0, 1, 4, 7, 14, 28 and 56 after treatment, 0.5ml of the water samples in duplicate was dispensed into the scintillation cups, mixed with 5 ml of scintillation liquid I (7 g of b-PBD, 0.6 g of POPOP and 110 g of naphthalene, made up to the volume of 1000 ml with dioxane), and determined in a liquid scintillation counter (Packard Tri-carb 2000 CA).

Soil: At day 0, 7, 14, 28, 56 and harvest, samples in triplicate were collected from the upper and lower layers of the paddy soil. They were dried and extracted 3 times with 20 ml of a solution composed of equal volume of acetone, methanol and benzene. 1 ml of the extract was mixed with 5 ml of the scintillation liquid I and counted for radioactivity.

Rice: At day 3, 7, 14, 28, 56 after transplantation and at harvest, rice plants were uprooted and divided into two parts, one above and one below the water line. The plant specimens were dried and extracted 3 times with 10 ml of a solution composed of equal volume of acetone, methanol and benzene. After filtering, 1 ml of the extract was mixed with 5 ml of the scintillation liquid I and counted. To estimate the residues in bound form, the plant specimens after extraction were burnt in a oxygen-flask and

the released ^{14}C was trapped with ethanoamine. Then, 1 ml of the trapped liquid was mixed with 5 ml of the cocktail II (6 g PPO + 0.3 g POPOP + 1000 ml dimethyl benzene) and counted.

Fish: Sampling was made at day 7, 14, 28 and 56 after releasing the fish into the tanks. In LRE, the fish pieces were digested with perchloric acid- hydrogen peroxide solution, mixed with scintillation liquid III (4 g of PPO + 445 ml of dehydrated alcohol + 555 ml of dimethyl benzene) and then counted. In ERE, the fish pieces were extracted with the mixture of equal volume of acetone, methanol and benzene. Then, the extract was mixed with scintillation liquid I and counted. The bound residues in fish body was also determined by the method as that for the rice plant.

The measurements were corrected for background radioactivity, recovery and quenching (using internal standard). The recovery rate was 97%, 96.5%, 95.2% and 88.7% for the soil extract, plant extract, burnt part of the plant and digested fish respectively. Apart from measurement using liquid scintillation counter, radioactivity in fish and early rice plant were also determined by autoradiography.

III. RESULTS AND DISCUSSION

The data listed in Table 1 to 6 indicate that the residues of the ^{14}C - carbofuran remained in the different components of the rice- fish ecosystem decreased with time.

Table 1

^{14}C - carbofuran retained in water in model rice- fish ecosystem

Sampling time (d)	LRE				ERE			
	Common dose		High dose		1x dose		2.5x dose	
	$\mu\text{ g/ml}$	%	$\mu\text{ g/ml}$	%	$\mu\text{ g/ml}$	%	$\mu\text{ g/ml}$	%
0	0.205	100	0.907	100	0.285	100	0.804	100
	± 0.008		± 0.057		± 0.006		± 0.042	
1	0.202	98.5	0.868	95.7	0.260	91.2	0.742	92.3
	± 0.007		± 0.069		± 0.005		± 0.087	
4	0.196	95.6	0.828	91.3	0.209	73.3	0.601	74.8
	± 0.005		± 0.067		± 0.009		± 0.026	
7	0.116	56.6	0.504	55.6	0.171	60.0	0.507	63.1
	± 0.002		± 0.015		± 0.009		± 0.040	
14	0.073	35.6	0.286	31.5	0.029	10.2	0.233	29.0
	± 0.001		± 0.006		± 0.005		± 0.044	
28	0.024	11.7	0.077	8.5	0.014	4.9	0.041	5.1
	± 0.001		± 0.004		± 0.004		± 0.006	
56	0.015	7.3	0.026	2.9	0.005	1.8	0.019	2.4
	± 0.001		± 0.004		± 0.001		± 0.003	

SE: Standard error

At day 56 after application with common dose, 7.3% and 1.8% of the pesticide were retained in the water of the LRE and ERE respectively (Table 1). The reduction rate of the ^{14}C - carbofuran in upper layer of the soil was higher than that of the lower layer

(Table 2 and 3). The chemicals and its degradative products in the rice plants increased (in terms of μ g chemicals/g rice plant) at the first stage, reached maximum levels during day 14 to 28 after application with common dose, and decreased thereafter (Table 4 and 5). The profile was similar to that of the high dose (2.5x) treatment (data omitted). At harvest, the pesticide residues remained in upper and lower parts of the late rice plants were 8.51 and 9.43 μ g/g in high dose treatment respectively, and were 18.68 and 17.69 μ g/g respectively in early rice plants. The residues in the ears were 1/8 to 1/12 of that in the other parts of the rice plants. The bound residues in the plants and fish bodies were higher than extractable fraction (Table 4, 5 and 6). Besides radiocounting, the ¹⁴C- carbofuran residues in plant and fish could be recorded by autoradiography through the experiments (Fig. 1 and 2).

Table 2
¹⁴C-carbofuran residues in the soil in model late rice- fish ecosystem

Sampling time (d)	Common dose (1x)				High dose (2.5x)			
	Upper layer		Lower layer		Upper layer		Lower layer	
	μ g/g	%	μ g/g	%	μ g/g	%	μ g/g	%
0	0.186	100	0.186	100	0.449	100	0.449	100
	± 0.001		± 0.001		± 0.011		± 0.011	
7	0.153	82.3	0.156	83.9	0.274	61.0	0.269	59.9
	± 0.028		± 0.028		± 0.018		± 0.011	
14	0.126	67.7	0.123	66.1	0.242	53.9	0.205	45.7
	± 0.007		± 0.007		± 0.024		± 0.007	
28	0.090	48.4	0.106	57.0	0.183	40.8	0.185	41.2
	± 0.007		± 0.008		± 0.011		± 0.012	
56	0.047	25.3	0.051	27.4	0.052	11.6	0.125	27.8
	± 0.008		± 0.003		± 0.002		± 0.010	
Harvest	0.030	16.1	0.047	25.3	0.050	11.1	0.084	18.7
	± 0.002		± 0.002		± 0.003		± 0.001	

Table 3
¹⁴C-carbofuran residues in the soil in model early rice- fish ecosystem

Sampling time (d)	Common dose (1x)				High dose (2.5x)			
	Upper layer		Lower layer		Upper layer		Lower layer	
	μ g/g	%	μ g/g	%	μ g/g	%	μ g/g	%
0	0.104	100	0.104	100	0.264	100	0.264	100
	± 0.003		± 0.003		± 0.026		± 0.026	
7	0.068	65.4	0.049	47.1	0.213	80.7	0.212	80.3
	± 0.001		± 0.001		± 0.005		± 0.015	
14	0.039	37.5	0.034	32.7	0.137	51.9	0.132	50.0
	± 0.001		± 0.001		± 0.001		± 0.001	
28	0.033	31.7	0.034	32.7	0.108	40.9	0.114	43.2
	± 0.001		± 0.002		± 0.007		± 0.006	
56	0.029	27.9	0.037	35.6	0.109	41.3	0.109	41.3
	± 0.011		± 0.001		± 0.006		± 0.008	
Harvest	0.025	24.0	0.028	26.9	0.099	37.5	0.107	40.5
	± 0.002		± 0.011		± 0.009		± 0.001	

Table 4
¹⁴C—carbofuran residues in late rice plants (1x)

Sampling time (d)	Upper part ^a (μ g/g)			Lowerpart ^a (μ g/g)		
	Extractable R. ^b	Bound R. ^c	Total	Extractable R. ^b	Bound R. ^c	Total
7	3.099 ±0.131	2.263 ±0.153	5.362 ±0.284	0.584 ±0.031	4.027 ±0.856	4.611 ±0.887
14	3.206 ±0.309	3.140 ±0.322	6.346 ±0.631	0.576 ±0.066	8.277 ±0.415	8.853 ±0.481
28	1.649 ±0.032	2.176 ±0.264	3.825 ±0.296	0.462 ±0.053	4.791 ±0.389	5.253 ±0.442
56	0.499 ±0.049	3.486 ±0.157	3.985 ±0.206	0.311 ±0.032	5.843 ±0.778	6.154 ±0.810
A(harvest)	0.405 ±0.044	3.506 ±0.065	3.911 ±0.109	0.274 ±0.021	5.047 ±0.329	5.321 ±0.349
B(harvest)	0.065 ±0.005	0.455 ±0.039	0.520 ±0.044	— — —	— — —	— — —

a: The portions of rice plants above or below the water line. b: Measured from the extractives. c: Measured from the plant specimens after extraction. A: In upper part of the plant, it contained the stems and leaves; In lower part, it contained the stems and roots of the rice plants. B: Ears of the rice plants.

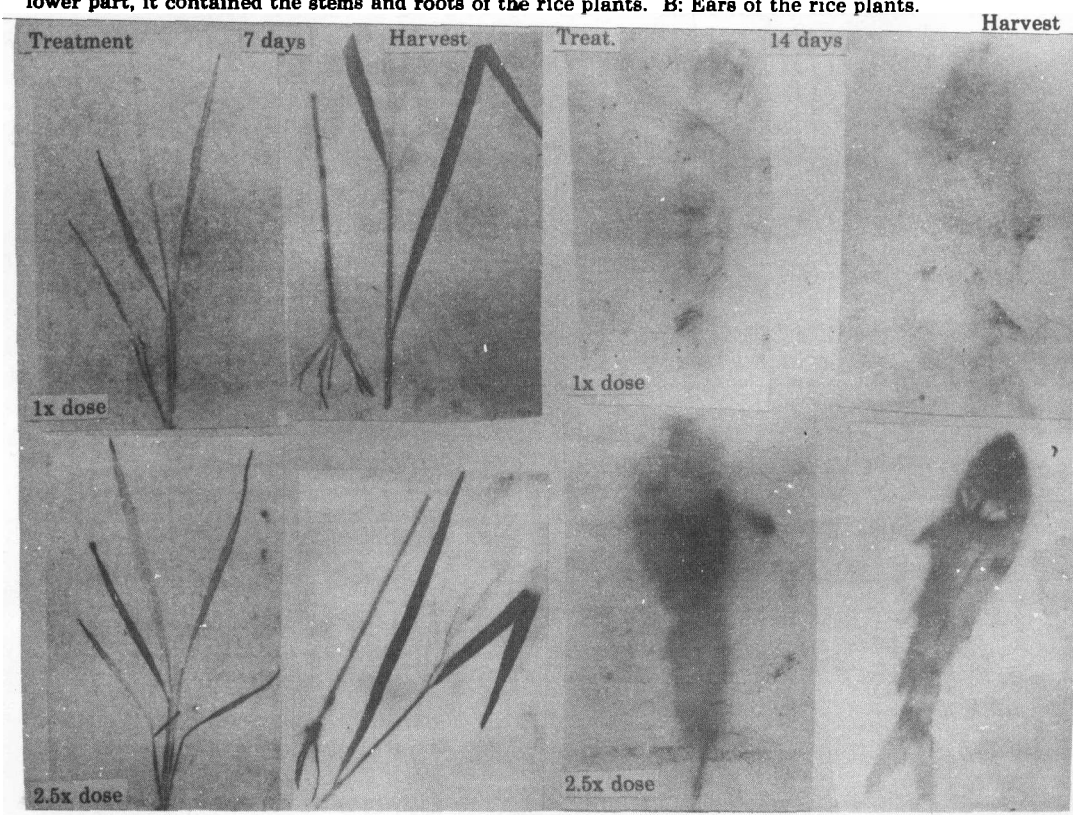


Fig.1 The autoradiograph of early rice plants after ¹⁴C—carbofuran treatment

Fig.2 The autoradiograph of fish body after ¹⁴C—carbofuran treatment

Table 5
¹⁴C—carbofuran residues in early rice plants (1x)

Sampling time (d)	Upper part (μ g/g)			Lower part (μ g/g)		
	Extractable R.	Bound R.	Total	Extractable R.	Bound R.	Total
3	0.976 ±0.070	0.926 ±0.111	1.902 ±0.181	0.410 ±0.027	1.149 ±0.301	1.559 ±0.328
7	1.076 ±0.129	2.838 ±0.494	3.914 ±0.623	0.418 ±0.034	2.468 ±0.530	2.886 ±0.564
14	1.364 ±0.237	4.660 ±0.344	6.024 ±0.581	0.423 ±0.029	8.499 ±1.337	8.922 ±1.366
28	1.553 ±0.082	3.932 ±0.335	5.485 ±0.417	0.432 ±0.014	9.378 ±0.807	9.810 ±0.821
56	0.422 ±0.044	2.743 ±0.425	3.165 ±0.469	0.297 ±0.012	6.212 ±0.433	6.509 ±0.445
A(harvest)	0.393 ±0.013	4.654 ±0.513	5.047 ±0.526	0.282 ±0.050	6.857 ±0.921	7.139 ±0.971
B(harvest)	0.047 ±0.010	0.517 ±0.070	0.564 ±0.080	— — —	— — —	— — —

Table 6
¹⁴C—carbofuran residues in fish in model early rice— fish ecosystem (μ g/g)

Sampling time (d)	Common dose (1x)			High dose (2.5x)		
	Extractable R.	Bound R.	Total	Extractable R.	Bound R.	Total
7	0.497 ±0.008	0.528 ±0.120	1.025 ±0.128	1.048 ±0.066	1.545 ±0.446	2.593 ±0.512
14	0.194 ±0.037	0.449 ±0.121	0.643 ±0.158	0.480 ±0.078	0.995 ±0.034	1.475 ±0.112
28	0.146 ±0.016	0.461 ±0.063	0.607 ±0.079	0.424 ±0.009	0.987 ±0.272	1.411 ±0.281
56	0.096 ±0.003	0.228 ±0.005	0.324 ±0.008	0.243 ±0.036	0.530 ±0.125	0.773 ±0.161
Harvest	0.109 ±0.003	0.276 ±0.005	0.385 ±0.008	0.146 ±0.004	0.353 ±0.006	0.499 ±0.010

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REFERENCES

[1] Chen Chuanqun, *Application of Atomic Energy in Agriculture (in Chinese)*, 4 (1983), 57.
 [2] Li Shengwu et al., *Fresh - Water Fishery (in Chinese)*, 1 (1984), 37.
 [3] Zhao Shanhuan, *Plant Protection*, 5 (1984), 17.
 [4] S.K.Ghosh, *Agr.*, 40 (1984), 97.
 [5] K.K.Mary et al., *J. Agr. Food Chem.*, 30 (1982), 1:116.
 [6] D.Freitag et al., *J. Agr. Food Chem.*, 32 (1984), 2:203.
 [7] S.U.Khan et al., *J. Agr. Food Chem.*, 32 (1984), 5:1189.
 [8] R.Siddarappa and I.Watanabe, *Bull. Envir. Contam. Toxic. (USA)*, 23 (1979), 544.