STUDY ON RESIDUES OF ^{14}C–FENITROTHION IN MODEL RICE–FISH ECOSYSTEM AND FIELD RICE–FISH ECOSYSTEM*

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ABSTRACT

Residues of ^{14}C-fenitrothion in a model rice-fish ecosystem and field rice-fish ecosystem were studied. When equal amounts of the pesticide were applied, the extractable residues in brown rice (equivalent to $34.3 \pm 1.9\,\mu g/kg$ fenitrothion) and rice stems and leaves ($20.9 \pm 1.5\,\mu g/kg$) of the model rice-fish ecosystem were 10—15 times higher than that of the field rice-fish ecosystem ($4.48 \pm 0.13\,\mu g/kg$ and $1.27 \pm 0.34\,\mu g/kg$ respectively). Residues in upper part of the soil (6.50 ± 0.1—$8.10 \pm 0.2\,\mu g/kg$) and lower part of the soil (1.30 ± 0.1—$1.50 \pm 0.1\,\mu g/kg$) of the model rice-fish ecosystem were 10—40 times higher than that of the field rice-fish ecosystem ($0.17 \pm 0.01\,\mu g/kg$). The extractable residues in paddy water of the model ecosystem ($0.30 \pm 0.01\,\mu g/kg$) were similar to that of the field ecosystem ($0.20 \pm 0.02\,\mu g/kg$). When the fenitrothion was sprayed on the rice plants, residues in brown rice, fish body, soil and paddy water were lower than those when the pesticide was sprayed on the surface of the soil.

Keywords Fenitrothion, Residue, Model, Field, Rice-fish ecosystem

1 INTRODUCTION

The pesticide fenitrothion is an effective chemical for protecting rice, trees, cotton *etc.* from a variety of insects and has been widely and effectively used in raising crops[1,3,4]. In order to examine the applicability of fenitrothion in the rice-fish ecosystem, a study of the residues in a model rice-fish ecosystem and in a field rice-fish ecosystem was carried out.

2 MATERIALS AND METHODS

2.1 Model rice—fish ecosystem

a. Glass tank The glass tanks are 120 cm × 90 cm × 50 cm. They were placed

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outdoors, surrounded with wire mesh and covered with glass to exclude predators and rainfall. The environmental conditions of the ecosystem including temperature, sunlight, humidity etc. were similar to those in natural field.

b. Soil Purple paddy soil collected from Sichuan Agricultural University Farm. It contained orgainc matter 2.95 %, silt 57.4 %, sand 16.18 %, clay 26.42 %, pH 6.1, was sieved through 10 mm mesh. 220 kg of the soil was put into each tank to a depth of 20 cm. At harvest, soil samples were collected from different points in the tanks. The soil columns were divided into two parts: upper (0—10 cm) and lower (10—20 cm) layer. They were dried at 60°C, crushed and sieved through the 0.5 mm mesh. 10 g of soil was extracted 3 times with a solution of dichloromethane+acetone (2:1) under continuous stirring for 30 min. After concentration, 1 ml of the extract was mixed with 5 ml of the scintillation liquid Ⅱ (7 g of b-PBD in 1000 ml of dioxane) and radioactivity was determined by a liquid scintillation counter (Packard Tricarb 2000 CA).

c. Rice Early season variety "Lu-Hong-Zhao" which matures in about 125 d was sown on 17 April, transplanted into the tanks on 17 May, 3 plants per hill, 24 hills per tank with a density of 16 cm × 17 cm, and harvested on 17 August.

Three hills of rice plants were sampled randomly. They were divided into four parts: root systems, stems and leaves, husks and brown rice. After drying at 60°C and grinding, 1 g of the specimen was transferred into a vial, mixed with 15 ml of benzene and allowed to stand overnight. The solution was then stirred for 1h, filtered, and 1ml of it was mixed with 5 ml of scintillation liquid Ⅱ, and the radioactivity was measured.

The residue of the rice plant after extraction was burnt in a oxidizer. The $^{14}CO_2$ released was trapped with ethanolamine, mixed with 3 ml of ethylene glycol ether and 5 ml of scintillation liquid Ⅲ (PPO 6 g, POPOP 0.3 g in 1000 ml of dimethyl benzene), and the radioactivity was determined.

d. Fish Twenty-four common carp (Cyprinus Carpio L.) 4.65 cm in length and 2.66 g in weight were put in each tank 19 d after transplantation.

At rice harvest, fish samples were collected, rinsed with tap water and weighed. The meat and bone were separated and chopped into small pieces. 250 mg was put into a test tube, mixed with 0.5 ml of $HClO_4$ and 1.6 ml of H_2O_2 and digested at 75°C for 2 h. After cooling, 0.3 ml of the solution was dispensed into vial, mixed with 5 ml of scintillation liquid Ⅲ, and the radioactivity measured.

e. Water After storing for more than one week, tap water with pH 6.6 was added into each tank. The level of the water was 3 cm at transplantation and 10 cm after the release of fish.

To determine the pesticide residue, 50 ml of the water in triplicate was collected from different parts of the tanks. The water samples were extracted with trichloromethane (3×30 ml), the extract was concentrated from 90 ml to 10 ml. One ml of the concentrated extract was dispensed in a scintillation vial, mixed with 5 ml of the scintillation liquid I (7 g of PBD, 0.6 g POPOP and 110 g of naphthalene in 1000 ml of dioxane) and radioactivity was determined.

The radioactivity remaining in the aqueous phase after extraction was also determined.

f. Pesticide The ^{14}C-fenitrothion (-^{14}C-dimethyl-) with specific activity 185 MBq / mmol (the radiopurity more than 90 %) was provided by the Shanghai Institute of Nuclear Research, the Chinese Academy of Sciences. Before application, it was dissolved in absolute ethyl alcohol and mixed thoroughly at a dilution of 1:1000 with 50 % fenitrothion emulsion produced in the Ling Bo Agrochemicals Plant.

Two application methods were used in the experiment: one was to spray the fenitrothion on the rice plants, and the other was to spray on surface of the soil. The treatments were carried out on the day 16th after transplantation (4 June) with same dose.

The counting data have been corrected for background, quenching and recovery. Counting error was kept below 5 %. The amount of pesticide residue was calculated based on the determination of a known amount of ^{14}C-fenitrothion in the samples.

2.2 Field rice—fish ecosystem

The soil, rice variety, density of the rice plants and environmental condition of the 9.2 m^2 field ecosystem were similar to that of the model ecosystem. There was no shelter over the field ecosystem, so the water within it could be renewed by rainfall. Sowing, transplantation, harvest and fish release in the field ecosystem were done at the same time as those in the model ecosystem. The same dose (111mg AI / m^2) of the 50 % non-radioactive fenitrothion emulsion (dilution 1:1000) was sprayed on the rice plants at days 2nd and 16th after releasing the fish. Forty common carps (average weight 1.95 g) were distributed into the ecosystem.

All the materials were sampled at rice harvest. Rice plants were divided into shoots (stems and leaves) and brown rice and smashed after being dried at 60°C. Fish samples collected were rinsed with tap water. Fish body (meat and bone) was chopped into small pieces after being weighed. All the samples were analyzed by the following procedures[2].

Shoot, brown rice and fish body: 5 g each was extracted with 50 ml of benzene and allowed to stand overnight, shaken for 1h, filtered through F_{3-4} glass funnel and washed 3 times with 5 ml of benzene. The filtrate was concentrated to 2 ml with a Kuderna-Danish concentrator.

Soil (upper soil): Anhydrous sodium sulfate (100 g) and 100 ml of a solution dichloromethane and acetone (2:1) were added to 50 g of soil, shaken for 1h and filtered. The residue was washed 3 times with 80 ml of the dichloromethane+acetone solution. The filtrate was concentrated to about 5 ml with a Kuderna-Danich concentrator.

Paddy water: 50 ml of paddy water was extracted twice with dichloromethane and the solution obtained was concentrated to 2 ml.

Purification of the concentrated solution: A Florisil column (inside diameter 1.5 cm) was washed with 20 ml of benzene or dichloromethane+ acetone. The concentrated solution was transferred to the column, and eluted with 100 ml of benzene or dichloromethane + acetone. The eluate was concentrated to less than 2 ml and analyzed for pesticide residues.

The equipment used was a Gc-9A gas chromatograph (Shmedzu Corp., Japan), equipped with an ECD-9 electron capture detector and a C-R3A data processor. Operating parameters were follows:

Chromatograph column: 3 mm × 2 m glass column, 1.5 % OV-17 and 2.0 % QF-1. Gas flow rate: N_2 60 ml/min. Temperature: column oven 220°C, injector 250°C.

3 RESULTS AND DISCUSSION

3.1 ^{14}C-Fenitrothion residue in the model rice-fish ecosystem

Residues of ^{14}C in the model rice-fish ecosystem at harvest are shown in Table 1. The data show that residues in the root system of the rice are higher than those in

Table 1

^{14}C residues in model rice-fish ecosystem expressed as fenitrothion

Item	Plant application			Soil application		
	Extractable / μg · kg^{-1}	Bound / mg · kg^{-1}	Total / mg · kg^{-1}	Extractable / μg · kg^{-1}	Bound / mg · kg^{-1}	Total / mg · kg^{-1}
Shoot	20.9 ± 1.5	2.47 ± 0.37	—	15.2 ± 0.7	2.26 ± 0.13	—
Root	52.1 ± 1.7	5.71 ± 0.33	—	52.5 ± 1.8	5.01 ± 0.12	—
Husk	13.1 ± 1.4	1.83 ± 0.35	—	18.3 ± 0.9	1.95 ± 0.19	—
Brown rice	34.3 ± 1.9	1.05 ± 0.21	—	45.8 ± 2.0	1.46 ± 0.03	—
Water	0.30 ± 0.01	0.008 ± 0.001	—	0.30 ± 0.01	0.012 ± 0.002	
Upper soil	6.50 ± 0.1	—	—	8.10 ± 0.2	—	—
Lower soil	1.30 ± 0.1	—	—	1.50 ± 0.1	—	—
Fish meat	—	—	1.10 ± 0.17	—	—	2.78 ± 0.34
Fish bone	—	—	0.92 ± 0.14	—	—	2.62 ± 0.55

Note: Bound residues in soil were not determined due to disfunction of the equipment.
Values are mean ± standard deviation

the shoots, husk and brown rice irrespective of the way that the pesticide was applied. Most residues in the rice plants exist in non-extractable bound form (> 96 %). Soil application results in higher residues in husk, brown rice, fish, paddy water and soil. Extractable residues in the upper part of the soil are 5 times higher than those in lower part of the soil. Residues in paddy water are lower than those in the other components of the ecosystem.

3.2 Fenitrothion residue in field rice—fish ecosystem

When the same dose of fenitrothion is applied, residues in different components of the field ecosystem are lower than those of the model ecosystem (Table 1 and 2). The

Table 2

Extractable residues of fenitrothion in field rice—fish ecosystem $\mu g \cdot kg^{-1}$

Shoot	Brown rice	Fish body	Upper soil	Water
1.27±0.34*	4.48±0.13	6.29±0.27	0.17±0.01	0.23±0.02

* Values are mean ± standard deviation

extractable risidues in the shoots and brown rice of the model ecosystem are 10 times higher than those of the field ecosystem. A similar difference could be seen in the soil of the two ecosystems. However, no significant difference was found between the water samples in the two ecosystems. The difference may be mainly due to the continuous renewal of the paddy water by rainfall in the field ecosystem.

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