

# STUDY ON BEHAVIOUR OF CR FORMULATION OF THIOBENCARB IN A MODEL PADDY FIELD\*

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## ABSTRACT

The fate of CR formulation of  $^{14}\text{C}$ -thiobencarb (thio.) was studied at the high rate of application in a model paddy field. Thio. could be released from the alginate formulation (TAL-17189) into water. The concentration of thio. in water increased with time, then declined. Thio. in water could be converted to more than 12  $^{14}\text{C}$ -degradation products which changed with time. An unknown degradation product ( $M_0$ ) was always prevailing after application. Thio. in water could be adsorbed by soil particles. Most of the adsorbed thio. retained in upper layer. Thio. in soil could be also degraded to more than 6 products. Thio. and its degradation products could conjugate with the compositions of soil to bound residues (BR). Thio. was 45.6% of the total  $^{14}\text{C}$ -extractable residues (ER) in upper layer soil at harvest.  $^{14}\text{C}$ -thio. in water and soil could be uptaken by rice plants. Thio. in plants existed in ER and BR. Most of  $^{14}\text{C}$ -residues in straw, roots, brown rice and husk were in bound form, more than 92% of the total  $^{14}\text{C}$  in them at harvest respectively. Thio. in plants could be metabolized to more than 9 metabolites which changed with time.  $^{14}\text{C}$ -thio. in straw, brown rice and husk accounted for 55.88, 6.06 and 11.18% of the total  $^{14}\text{C}$ -ER of them at harvest respectively. An unknown  $^{14}\text{C}$ -metabolite in brown rice was prevailing, accounted for 63.03% of the total  $^{14}\text{C}$ -ER.

**Keywords** Thiobencarb, Controlled-release formulation, Paddy field

## 1 INTRODUCTION

Thiobencarb, S-(4-chlorobenzyl) N, N-diethyl-thiocarbamate is one of the common used herbicides in rice field of Asian countries and areas. Degradation of thiobencarb in soil, uptake and translocation of thiobencarb by plants and photodegradation of benthocarb *etc.* had been studied<sup>[1-3]</sup>.

It is now well recognized that controlled-release (CR) formulations of pesticides have many advantages over the common formulation, such as reducing the

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environmental loss and contamination of pesticides, increasing efficiency *etc.* Recent years, research on the application of CR technique to formulations of herbicide is receiving attention. The CR formulations of herbicide thiobencarb have been prepared by M. Hussain *et al*<sup>[4]</sup>. The release of butachlor, oxadiazon and thiobencarb herbicides from CR formulations have been studied by Sun Jinhe and Hussain M *et al.* respectively<sup>[4-6]</sup>.

It is very important to study the residues, metabolism and degradation of CR formulation of thiobencarb in rice field to evaluate the safety of CR formulation of thiobencarb after application. This paper presents the behaviour of alginate formulation of thiobencarb in a model paddy field which was studied using nuclear techniques.

## 2 MATERIALS AND METHODS

### 2.1 Chemicals

<sup>14</sup>C-thiobencarb alginate formulation (TAL-17189) (specific activity: 201.8 kBq / g; 5.78 a. i. %), the structure of thiobencarb is shown in Fig.1; the commercial formulation (Saturn, 10 % G); reference standards: thiobencarb (99 %); desethyl thiobencarb, 4-chlorobenzoic acid and 4-chlorobenzyl methyl sulfone > 96 %; all the solvents used in the study were of analytical grade.

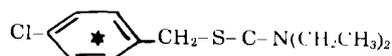


Fig.1 Structural formula of thiobencarb

Asterisk indicates <sup>14</sup>C

### 2.2 Paddy soil and rice plant

Paddy soil was taken from the experimental farm of Zhejiang Agric. Univ. (organic matter content 0.8 %; pH 7.6; cation exchange capacity (mmol / 100g soil) 20.47; mechanical analysis (<0.01 mm 9.3 %). Rice seedlings: Zhejiang-852).

### 2.3 A model paddy field

Paddy soil (wet) was placed in two pools (1 m × 1 m) under the natural condition<sup>[7]</sup>. Twenty four of the soil sampling tubes (2 cm × 22 cm) made of stainless steel net were buried into soil in each pool. Tap water was added into each pool to incubate for 10 days and soil was 22 cm in height.

Twenty five hills of seedling (8 seedlings / hill) were transplanted into two pools respectively. <sup>14</sup>C-thiobencarb alginate formulation was evenly broadcasted in a pool at 9 kg a.i. / ha ( I ) next day.

One week after transplanting, 10 % G of thiobencarb was applied in the other pool ( II ) at the same dose as in I , and <sup>14</sup>C-thiobencarb alginate formulation was applied in I at 4.5 kg a.i. / ha again after the first batch of water and soil samples were taken. The paddy water levels in both of I and II were maintained at 1 cm. 4 weeks and 7 weeks after transplanting, water levels were then raised to 3 cm and

4.5 cm, respectively.

## 2.4 Sampling and analysis

Water and soil samples were taken 6, 14, 21, 28, 49 and 91 days (harvest) after the first application respectively. Plant samples were taken 14, 21, 28, 49 and 91 days (harvest) after the first application.

### 2.4.1 Water

Paddy water ( $0.2\text{ ml} \times 3$ ) samples from 1 were taken and counted by a liquid scintillation counter (LSC, model packard 1900TR) using 10 ml of a toluene based cocktail (PPO: POPOP: toluene: 2-ethoxy ethanol = 5 g: 0.4 g: 700 ml: 550 ml). The counting efficiency was corrected by the external channel ratio method, and the counting errors were controlled below 5%. Meanwhile 20 ml of water samples in 1 were taken in duplicate, extracted 3 times with equal volumes of ether, the aqueous phase was acidified to pH 1.0 with respect to hydrochloric acid, extracted 2 times as above<sup>[3]</sup>. The volumes of the aqueous phase were measured and 0.5 ml of aliquots (in duplicate) were counted by LSC as above. The combined ether phase was concentrated, dried under air condition, then dissolved with methanol. For identification of the degradation products, the methanol solutions were co-chromatographed on silica gel GF<sub>254</sub> (E. Merk) plates with reference standards. Benzene-ethyl acetate (10:1 v/v) was used as a developing solvent system<sup>[1]</sup>. The reference standards were located under UV lamp at 254 nm. The developed plates were exposed to X-ray films for 126 d. The spots on the plates were directly scraped into counting vials for quantification by LSC as above.

### 2.4.2 Soil

Three soil sampling tubes were removed from 1, and the soil were divided into two sections. Air-dried, crashed, mixed and the upper layer of soil ( $24\text{ g} \times 6$ ) were extracted. The extracts were counted by LSC as above. The remainder was concentrated to dry, dissolved with n-hexane, chromatographed on a Florisil column. <sup>14</sup>C-thiobencarb and its degradation products were eluted by n-hexane-ether (7:1 v/v)<sup>[8]</sup>. The eluates were analysed using TLC and radioautography exposing for 110 d as for water. The <sup>14</sup>C remaining in the extracted soil and <sup>14</sup>C in the lower layer of soil were determined by combustion and counting<sup>[9]</sup>.

### 2.4.3 Plants

Two hills of rice plants were randomly sampled from 1<sup>[6]</sup>. The samples were extracted to get extractable residues (ER) and counted as soil. The remainder was concentrated, cleaned up and analysed, the extracted residues were combusted, counted *et al.*, using the same ways as soil.

### 2.4.4 At harvest

Paddy water ( $90\text{ ml} \times 2$ ) and six sampling tubes from 1 were taken, extracted, counted and analysed *et al.*, as described above.

All of plants were cut along the water surface, divided to straw, roots, brown rice and husk. All of the samples were dried at 40–50°C, milled to powder for extraction, the extracts and residues were counted, analysed *et al.*, as above.

### 3 RESULTS AND DISCUSSION

Although the growth of rice plants in I at the high rate of application of alginate formulation of  $^{14}\text{C}$ -thiobencarb was similar to that in II at the high rate of application of the commercial formulation of thiobencarb, the height of plants was slightly shorten.

The behaviour of thiobencarb released from alginate formulation in I was as follows.

#### 3.1 In water

The results of dissipation and transformation of  $^{14}\text{C}$ -thiobencarb are listed in Table 1. Figures in Table 1 show that the concentration of thiobencarb in water increased with time, then decreased and was the highest and the lowest 28 d and 91 d (at harvest) after the first application, respectively.  $^{14}\text{C}$ -thiobencarb in water could be transformed into water soluble products.

We attribute the results described above to the fact that the amount of  $^{14}\text{C}$ -thiobencarb released from alginate formulation increased with

time, thiobencarb in water could be adsorbed by soil particles, absorbed by plants, hydrolysed and photolysed *etc.*

The results of identification of  $^{14}\text{C}$ -compounds in organic phase are shown in Table 2. Most of  $^{14}\text{C}$ -thiobencarb in organic phase were converted into more than 12  $^{14}\text{C}$ -degradation products. Among them, an unknown polar  $^{14}\text{C}$ -product ( $M_o$ ) at the original spot on plate was prevailing. They ( $M_o$ ) were 37.31, 56.85, 61.59, 96.52, 46.15 and 18.48 % of the total  $^{14}\text{C}$  detected in organic phase 6, 14, 21, 28, 49 and 91 d after the first application respectively.  $^{14}\text{C}$ -thiobencarb was 44.27 % of the total  $^{14}\text{C}$  in organic layer at harvest which explain that the degradation products of thiobencarb lost easily.

#### 3.2 In soil

**Table 1**  
Residues and transformation of  $^{14}\text{C}$ -thiobencarb released from alginate formulation in paddy water<sup>a</sup>

Time <sup>b</sup> / d	$W_o$ <sup>c</sup>	Water phase	Organic phase <sup>d</sup>
		$R_w$	$R_o$
6	2.167 ± 0.085	0.343 ± 0.040	1.824
14	3.295 ± 0.079	0.185 ± 0.011	3.110
21	3.000 ± 0.105	0.086 ± 0.000	2.762
28	5.229 ± 0.183	0.295 ± 0.010	4.933
49	3.114 ± 0.000	1.229 ± 0.019	1.885
91 (harvest)	0.781 ± 0.039	0.433 ± 0.021	0.348

a: Figures were expressed in  $^{14}\text{C}$ -thiobencarb and in  $\mu\text{g}/\text{ml}$ . b: Time = Days after the first application; the second application was conducted 6 days after the first application and after the first sampling. c:  $W_o$  = Total  $^{14}\text{C}$  detected in water samples. d:  $R_o = W_o - R_w$

The pattern of residues and distribution of  $^{14}\text{C}$ -thiobencarb in soil is listed in Table 3. Thiobencarb adsorbed by soil particles increased with time, most of the

**Table 2**  
**Results of analysis of  $^{14}\text{C}$ -compounds in the organic phase of water samples<sup>a</sup>**

$^{14}\text{C}$ - compounds	Time after the first application / d					
	6	14	21	28	49	91
Thiobencarb (parent)	6.13	6.89	5.75	—	8.22	44.27
Desethyl thiobencarb	6.48	3.18	t	—	4.51	4.36
4-Chlorobenzyl methyl sulfone	17.59	5.15	6.65	—	5.57	t
4-Chlorobenzoic acid	13.76	7.27	6.55	t	7.43	t
<b>Unknown compounds<sup>b</sup></b>						
M <sub>0</sub>	37.31	56.85	61.59	96.52	46.15	18.48
M <sub>1</sub>	—	—	—	—	5.57	—
M <sub>3</sub>	t	4.16	3.43	—	5.31	t
M <sub>4</sub>	5.56	t	4.23	—	4.51	t
M <sub>5</sub>	4.46	t	t	—	t	—
M <sub>6</sub>	t	t	t	—	3.98	5.34
M <sub>7</sub>	t	t	t	—	3.98	8.29
M <sub>8</sub>	t	t	t	—	4.77	10.33
M <sub>9</sub>	—	5.90	t	—	—	—
M <sub>10</sub>	—	t	—	—	—	—

a: Total  $^{14}\text{C}$  detected in the organic phase was 100 %; —: Not detected (<1 %); t: Trace (<3 %); b: M<sub>0</sub>: At the original spot on the TLC plates

**Table 3**  
**Extractable and bound residues of  $^{14}\text{C}$ -thiobencarb released from alginate formulation in soil\***

Time / d	Upper layer soil				Lower layer soil (total)	% of the upper layer in total $^{14}\text{C}$ in soil
	E	B	T	B/T(%)		
6	0.633 ± 0.051	1.557 ± 0.116	2.190	71.10	1.348 ± 0.202	61.90
14	1.095 ± 0.058	1.281 ± 0.056	2.376	53.91	1.429 ± 0.205	62.44
21	2.710 ± 0.325	1.591 ± 0.081	4.300	36.98	2.152 ± 0.041	66.65
28	1.310 ± 0.060	1.714 ± 0.075	3.024	56.68	1.952 ± 0.082	60.77
49	1.671 ± 0.160	3.795 ± 0.140	5.466	69.43	1.691 ± 0.079	76.37
91 (harvest)	2.181 ± 0.200	5.086 ± 0.117	7.267	69.99	1.530 ± 0.140	82.58

\* Figures were expressed in  $^{14}\text{C}$ -thiobencarb and in  $\mu\text{g/g}$ ; E = Extractable residues; B = Bound residues; T = B + E.

adsorbed thiobencarb retained in the upper layer. Some of  $^{14}\text{C}$ -thiobencarb in soil could be converted into the degradation products. Such conversions may be proceed on the pathways due to light, temperature and pH, or the inorganic chemical composition of soil. Some of conversions were carried out by the microorganisms of soil. Some of  $^{14}\text{C}$ -thiobencarb or its degradation products could be conjugated with the compositions of soil to form bound residues (BR).  $^{14}\text{C}$ - BR in the upper layer of

soil were prevailing.

The results of identification of  $^{14}\text{C}$ -ER using TLC and radioautography are shown in Table 4. The results express that most of  $^{14}\text{C}$ -compounds in  $^{14}\text{C}$ -ER were the parent thiobencarb except an unknown polar  $^{14}\text{C}$ -degradation product  $M_0$  at the original spot on the TLC plate,  $^{14}\text{C}$ -thiobencarb and  $M_0$  were 45.61 % and 49.67 % of the total  $^{14}\text{C}$  in  $^{14}\text{C}$ -ER at harvest respectively.

**Table 4**  
**Results of analysis of  $^{14}\text{C}$ -compounds in  $^{14}\text{C}$ -ER of the upper layer soil\***

$^{14}\text{C}$ - compound	Time after the first application / d					
	6	14	21	28	49	91
Thiobencarb	92.87	98.20	97.66	89.85	93.02	45.61
Desethyl thiobencarb	—	—	t	t	t	t
4-chlorobenzoic acid	—	—	—	t	—	—
Unknown compounds						
$M_0$	t	—	—	t	t	49.67
$M_1$	—	—	—	t	—	—
$M_2$	3.49	—	—	t	—	—
$M_3$	—	—	—	t	—	—
$M_6$	—	—	—	—	t	t

\* Total  $^{14}\text{C}$  detected in  $^{14}\text{C}$ -ER was 100 %; —: Not detected (<1 %); t: Trace (<3 %)

**Table 5**  
**Extractable and bound residues of  $^{14}\text{C}$ -thiobencarb in plants<sup>a</sup>**

		Time after the first application / d				
		14	21	28	49	91(harvest)
Stem + leaves	E	17.80 ± 1.48	31.62 ± 4.74	23.06 ± 1.84	17.35 ± 2.42	1.85 ± 0.27
	B	26.64 ± 0.69	25.69 ± 0.43	22.36 ± 0.76	28.45 ± 3.12	23.38 ± 1.58
	T	44.44	57.31	45.42	45.80	25.23
	B/T(%)	59.95	44.83	49.23	62.12	92.67
Roots	E	32.72 ± 0.88	28.78 ± 0.15	34.13 ± 2.62	44.10 ± 2.21	8.76 ± 0.61
	B	23.55 ± 2.59	23.59 ± 1.43	46.17 ± 1.01	54.38 ± 3.20	190.78 ± 14.88
	T	56.27	52.37	80.30	98.48	199.54
	B/T(%)	41.85	45.04	57.50	55.22	95.61
Brown rice	E					0.65 ± 0.07
	B					(1.62 ± 0.14) <sup>b</sup>
	T					22.22 ± 2.03
	B/T(%)					(40.70 ± 1.91)
	T					22.87 (42.32)
	B/T(%)					97.16 (96.17)

a: Figures were expressed in  $^{14}\text{C}$ -thiobencarb and in  $\mu\text{g/g}$ , and calculated in fresh weight of samples; b: Figures in the parentheses indicated residues in husk

### 3.3 In plants

$^{14}\text{C}$ -thiobencarb in water and soil could be uptaken by plants and translocated

into whole plant.  $^{14}\text{C}$ -thiobencarb in plants were in extractable and bound forms. The dynamics of  $^{14}\text{C}$ -ER and  $^{14}\text{C}$ -BR in plants are listed in Table 5. The concentration of  $^{14}\text{C}$ -residues in roots was higher than that in straw (stem+leaves). Most of  $^{14}\text{C}$ -residues in straw, roots, brown rice and husk were in bound form, more than 92 % of the total  $^{14}\text{C}$  in them at harvest.

The results of analysis of  $^{14}\text{C}$ -compounds in  $^{14}\text{C}$ -ER of plants are shown in Table 6 and 7.

Table 6

Results of analysis of  $^{14}\text{C}$ -compounds in  $^{14}\text{C}$ -ER of straw (stem+leaves), brown rice and husk

$^{14}\text{C}$ -compound	Time after the first application / d						
	14	21	28	49	91	91	
	Straw (stem+leaves)				Brown rice	Husk	
Thiobencarb	72.13	3.27	82.33	49.17	55.88	6.06	11.18
Desethyl thiobencarb	4.22	—	t	t	—	6.97	24.12
4-chlorobenzyl methyl sulfone	—	—	—	t	—	—	7.06
4-chlorobenzoic acid	4.37	3.41	t	6.18	—	t	—
Unknown compounds							
M <sub>0</sub>	10.54	89.14	t	12.35	35.29	18.48	9.41
M <sub>1</sub>	t	t	t	6.65	—	63.03	5.88
M <sub>2</sub>	—	—	—	t	—	t	4.12
M <sub>3</sub>	—	—	—	t	—	—	10.00
M <sub>4</sub>	—	—	—	3.30	—	t	7.65
M <sub>5</sub>	t	—	—	—	—	—	8.82
M <sub>6</sub>	4.92	—	7.37	3.56	8.82	—	11.76

Notice: In Table 6 and 7, total  $^{14}\text{C}$  detected in  $^{14}\text{C}$ -ER was 100 %; —: Not detected (<1 %); t: Trace (<3 %)

Table 7

Results of analysis of  $^{14}\text{C}$ -compounds in  $^{14}\text{C}$ -ER of roots

$^{14}\text{C}$ -compound	Time after the first application / d				
	14	21	28	49	91 (harvest)
Thiobencarb	86.18	52.76	87.11	85.06	59.33
Desethyl thiobencarb	3.84	t	4.74	4.93	3.83
4-chlorobenzyl methyl sulfone	—	—	—	—	t
4-chlorobenzoic acid	t	t	—	t	t
Unknown compounds					
M <sub>0</sub>	t	41.77	t	t	3.88
M <sub>3</sub>	t	—	—	—	—
M <sub>4</sub>	—	—	—	—	t
M <sub>5</sub>	—	—	t	t	27.0
M <sub>6</sub>	t	—	t	t	t
M <sub>7</sub>	—	—	t	—	—

Thiobencarb in straw (stem+leaves), roots, brown rice and husk could be

metabolized to many metabolites which changed with time (Table 6). At harvest,  $^{14}\text{C}$ -thiobencarb in straw, brown rice and husk accounted for 55.88, 6.06 and 11.18 % of the total  $^{14}\text{C}$ -ER of them respectively. An unknown  $^{14}\text{C}$ -metabolite ( $M_1$ ) in brown rice was prevailing, accounted for 63.03 % of the total  $^{14}\text{C}$ -ER (Table 6).

$^{14}\text{C}$ -thiobencarb in roots could be also metabolized to many metabolites. Most of  $^{14}\text{C}$ -compounds in  $^{14}\text{C}$ -ER were parent, thiobencarb (Table 7). At harvest, an unknown compound  $M_5$  accounted for 27.0 % of the total  $^{14}\text{C}$ -ER.

#### 4 CONCLUSIONS

Thiobencarb could be released from CR formulation into water after the alginate formulation of  $^{14}\text{C}$ -thiobencarb (thio.) was applied in a model paddy field, the concentration of thio. in water increased with time, then declined. Thio. in water could be adsorbed by soil particles. Most of the adsorbed thio. retained in upper layer. Thio. in water and soil could be uptaken by plants and translocated into whole plants.

Thio in water could be degraded to more than 12 degradation products. Thio. in soil and plants could be also degraded and metabolized to many degradation products and metabolites which changed with time. Most of  $^{14}\text{C}$ -residues in straw, roots, brown rice and husk were in bound form at harvest respectively.

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#### REFERENCES

- 1 Ishikawa K, Nakamura Y, Kuwatsuka S. *J Pestic Sci*, 1976; 1:49
- 2 Nakamura Y, Ishikawa K, Kuwatsuka S. *Agr Biol Chem*, 1974; 38:1129
- 3 Ishikawa K, Nakamura Y, Niki Y *et al.* *J Pestic Sci*, 1977; 2:17
- 4 Hussain M, Gan J Y, Nasir Rathor M. *Pestic Sci*, 1992; 34:341
- 5 Sun Jinhe, Li Xingming, Chen Ziyuan *et al.* *Nuclear Science and Techniques*, 1991; 2:199
- 6 Sun Jinhe, Gan Jianying, Li Xingming *et al.* *Acta Agriculture Nucleatae Sinica*, 1991; 5:120
- 7 Sun Jinhe, Li Xingming, Chen Dafu *et al.* *J Zhejiang Agricultural University*, 1993; 19:104
- 8 Mo T, Chen H X, Lu Y T. *Method of residues analysis of pesticides (in Chinese)*. Shanghai Science and Technology Press, 1992
- 9 Sun Jinhe, Gan Jianying, Chen Ziyuan. *Pestic Sci*, 1989; 26:147