

Degradation of thiobencarb in anaerobic soils

(Degradasi thiobencarb di dalam tanah anaerob)

U. B. Cheah* and D. G. Crosby**

Key words: thiobencarb, degradation, anaerobic soils

Abstrak

Kadar dan hasilan degradasi thiobencarb di dalam tiga jenis tanah California telah dikaji. Penyahklorinan racun herba di dalam tanah juga diselidiki. Kajian makmal dengan menggunakan ^{14}C -thiobencarb dalam ekosistem akuatik tanah-air menunjukkan bahawa kadar penguraian racun herba yang perlahan dalam keadaan anaerob. Kebanyakan (37–44%) thiobencarb yang digunakan berada di dalam air sehingga 45 hari selepas perlakuan. Racun herba yang didapati sekata pengumpulannya di dalam tanah menunjukan kadar degradasi yang perlahan. Hasilan degradasi utama ialah 4-klorobenzil alkohol, 4-asid klorobenzoik dan desethylthiobencarb. Pembentukan thiobencarb nyahklorin yang dilaporkan bersifat fitotoksik kepada pokok padi tidak ditemui di dalam tanah dengan atau tanpa penambahan jerami padi.

Abstract

The rate and products of degradation of thiobencarb in three types of Californian soils under anaerobic conditions were examined. Dechlorination of the herbicide in the soils was also investigated. A laboratory study using ^{14}C -thiobencarb in a soil-water aquatic ecosystem showed a slow rate of dissipation of the herbicide in anaerobic soils. Much (37–44%) of the applied thiobencarb remained in the water 45 days after treatment. A steady build-up of the herbicide concentration in the soils was observed, suggesting a slow rate of degradation. Major degradation products were 4-chlorobenzyl alcohol, 4-chlorobenzoic acid and desethylthiobencarb. The formation of dechlorinated thiobencarb, reported to be phytotoxic to rice plants, was not evident in the soils, with or without augmentation with rice straw.

Introduction

Thiobencarb (benthiocarb, *S*-4-chlorobenzyl *N*, *N*-diethylthiocarbamate) has been widely used in many countries for the control of various weeds, especially barnyard grass, in the cultivation of rice. Application of this herbicide has resulted in phytotoxicity to rice plants in a few instances, attributed to the dechlorinated thiobencarb, *S*-benzyl *N*,

N-diethylthiocarbamate (Ishikawa et al. 1976); however, this dwarfing of rice was reported in a limited number of rice fields, and only under specific conditions (Moon and Kuwatsuka 1984). A number of other thiobencarb degradation products have also been detected in soils from treated fields, mainly through laboratory studies (Ishikawa et al. 1976; Ishikawa et al. 1980; Moon and

*Basic Research Division, Headquarters Station, MARDI Serdang, P.O. Box 12301, 50774 Kuala Lumpur, Malaysia

**Department of Environment Toxicology, University of California 95616, Davis, California, USA

Authors' full names: Cheah Uan Boh and D. G. Crosby

©Malaysian Agricultural Research and Development Institute 1996

Kuwatsuka 1984; Ross and Sava 1986; Braverman et al. 1990). In California, incidents of rice injury have been reported although thiobencarb was not implicated at the time.

The objectives of this laboratory study were to determine the rate and products of degradation of thiobencarb in three different submerged rice-field soils, including the possibility of reductive dechlorination to the phytotoxic product.

Materials and methods

Radioactive thiobencarb

¹⁴C-Thiobencarb (4-chlorobenzyl *N*, *N*-diethylthiocarbamate, Chevron Chemical Co.) was uniformly-labelled in the benzene ring. The specific activity was 3.83 mCi/mmole, and radiochemical purity was 100%.

Chemicals

Thiobencarb, 100% pure, and desethylthiobencarb, 98.9% pure, were obtained from Chevron Chemical Co., Richmond, California. 4-Chlorobenzoic acid, m.p. 239 °C, and 4-chlorobenzyl alcohol were purchased from Aldrich Inc., Milwaukee, Wisconsin.

Soils

Three different types of Californian soils, San Joaquin loam, Willows clay and Stockton Adobe clay, were collected from rice fields on 11 April 1991. The soils, passed through a 2-mm sieve with the addition of deionized water, were incubated for 14 days prior to treatment with radiolabelled thiobencarb. Analysis of the soil samples was carried out.

The soils were oven dried at 100–105 °C to determine the moisture content. The moisture contents for Willows clay 1 and 2, San Joaquin loam 1 and 2 as well as Stockton Adobe clay 1 and 2 were 39.2, 26.4, 14.1, 6.5, 15.5 and 18.0% respectively.

Degradation

Soil samples (75 g wet weight) were placed in glass test tubes (3.5 cm diameter, 22.5 cm length) fitted with a 24/40 ground glass joint and incubated under a 5-cm layer of deionized water (60 mL) at 20 °C for 14 days prior to treatment with radiolabelled thiobencarb (Marvel et al. 1978). A tube containing glass wool, a polyurethane foam plug and Drierite (4 cm) was attached to each test tube. A column of Ascarite (5 mg) was attached through a rubber stopper to the top of each of these test tubes for each of the three different types of soils to allow for the determination of evolved carbon dioxide at the end of the experiment. Three replicate tubes were removed at regular intervals for the sampling of water, soil and foam.

A similar system was established to investigate dechlorination of thiobencarb in soils. Six types of soils, non-amended and amended with rice straw (0.5 g), were used. The soils (35 g) were submerged under deionized water (30 mL) in glass test tubes (3.8 cm diameter, 14 cm length) and incubated for 14 days prior to treatment with thiobencarb. The tubes, sealed with glass stoppers and aluminium foil, were allowed to stand for 40 days before sampling.

Thiobencarb treatment

Labelled thiobencarb (0.552 µCi) was applied to each of the glass tubes, augmented by non-labelled material to provide a final concentration of 10 mg/kg in the soil. Only non-labelled thiobencarb was used in the dechlorination study to give a similar concentration of 10 mg/kg.

At intervals up to 45 days, the polyurethane foam plug was transferred via forceps to a glass tube and extracted twice with acetone (20 mL). The extracts were decanted, combined and evaporated on a rotary evaporator to a small volume (2 mL). An aliquot (0.5 mL) was transferred by micropipette to a scintillation vial for radioassay with a liquid scintillation counter (Packard Tricarb 2000CA Model, Packard Instrument Co.).

The aqueous layer in the tube was decanted, filtered and extracted onto a solid-phase extraction (SPE) cartridge (C18, Varian Analytichem Bond Elut). An aliquot (0.5 mL) of the ethyl acetate eluate (2 mL) was radioassayed.

The remaining soil was placed in a beaker (300 mL) and extracted with acetone (3 x 100 mL) by shaking for 2 h on a horizontal shaker (Eberbach Corp., Ann Arbor, Michigan). The aqueous acetone extracts were decanted and combined, acetone removed through evaporation. The remaining aqueous phase extracted with SPE and the eluate radioassayed as described previously.

The extracted soil was air-dried and the activity of the bound residues determined by combustion of an aliquot (250 mg) in an oxidizer (Packard Tricarb Oxidizer) and liquid scintillation counting. ^{14}C -Carbon dioxide was released from the Ascarite and trapped in 0.25 M NaOH solution (30 mL). This was achieved by placing the Ascarite in a three-neck boiling flask and injecting concentrated hydrochloric acid through a septum in the middle neck until a yellow colour was obtained. A continuous flow of nitrogen was introduced from another neck and the generated carbon dioxide swept out through the third opening. An aliquot (1.0 mL) of the NaOH solution was radioassayed.

^{14}C -Recovery

^{14}C -Thiobencarb was added separately to polyurethane foam, water and soils; extraction was carried out as described, and radioactivity determined. The recovery was found satisfactory for the analytical procedure employed (*Table 1*).

Thin layer chromatography

The extracts (100 μL) of foam, water, and soil were spotted on TLC plates (Silica Gel 60 F254, precoated, 20 x 20 cm, layer thickness 0.25 mm). Standard solutions of 4-chlorobenzyl alcohol, 4-chlorobenzoic acid and desethylthiobencarb also were

Table 1. Percentage recovery of ^{14}C -thiobencarb

Matrix	Replication			Average
	I	II	III	
Water	72.5	75.1	79.6	75.7
Soil	69.7	76.8	72.3	72.9
Foam	92.5	89.5	93.2	91.8

spotted on the sample plate. The plates were developed in a solvent mixture of chloroform: diisopropyl ether: n-hexane: acetic acid (10:10:10:1) and examined on a TLC plate scanner (Bioscan System 200 Imaging Scanner).

Results and discussion

The dissipation of thiobencarb from water was rather slow; between 37% and 44% remained in the water 45 days after treatment (*Table 2*). Ross and Sava (1986), however, showed a much faster disappearance of the herbicide from water in rice fields; thiobencarb residues dropped from a highest level of 580 $\mu\text{g/L}$ at 4 days after treatment to 56 $\mu\text{g/L}$ at 16 days of treatment, a 90% decrease in the concentration in less than 2 weeks. Other studies also indicated a shorter half-life (6–9 days) of thiobencarb in field water (Yusa and Ishikawa 1977). The difference in the observed results may be attributed to the almost closed system of the laboratory test, where the influence of other environmental factors such as air movement was absent.

The rate of degradation of thiobencarb also was observed to be slow in soils. There was no significant difference in the rate among the three types of soils; indeed, there was a slow increase of the soil concentration of thiobencarb due to adsorption from the water. Similar results were observed by Ross and Sava (1986) in their field studies; they showed that thiobencarb residues dropped from a peak level of 3.9 mg/kg at 4 days after treatment to 2.3 mg/kg at 32 days. In our laboratory studies, 44–46% of the thiobencarb (extractable and non-extractable) applied remained in the soil 45 days after treatment.

Table 2. Distribution of ^{14}C in water, soil, polyurethane foam, and evolved CO_2

Soil type	Matrix	% of applied ^{14}C at 5 intervals (days after application)				
		0	10	22	35	45
Willows clay	Water	81.7	65.6	55.9	58.0	41.1
	Soil (e)	6.8	14.5	23.9	29.9	31.6
	(ne)	2.4	6.3	6.6	14.3	15.2
	Foam	nd	1.0	3.8	5.3	3.4
	CO_2	ns	ns	ns	ns	0.18
	Total	90.9	87.4	90.2	107.5	91.5
San Joaquin loam	Water	79.4	70.3	54.3	46.4	37.0
	Soil (e)	5.7	14.9	21.6	32.7	37.4
	(ne)	3.5	4.5	4.4	6.1	7.1
	Foam	nd	0.58	1.1	1.8	3.0
	CO_2	ns	ns	ns	ns	0.12
	Total	88.6	90.3	81.4	87.0	84.6
Stockton Adobe clay	Water	83.4	74.5	70.5	53.3	44.2
	Soil (e)	9.5	16.7	20.8	30.1	33.2
	(ne)	2.2	4.1	4.8	18.6	15.2
	Foam	nd	0.8	2.6	3.3	2.9
	CO_2	ns	ns	ns	ns	ns
	Total	95.1	96.1	98.7	105.3	95.5

e = extractable

nd = radioactivity not detectable

ne = non-extractable

ns = not sampled

Our results also showed a high percentage of non-extractable radioactivity in the soil, which appeared to increase with increasing concentration of the compound and increasing clay content. Low microbial activity was evident from the low carbon dioxide recovery from the Ascarite trap (0.12–0.18% of the thiobencarb applied). This may partly contribute to the persistent behaviour of thiobencarb in anaerobic soils. The low radioactivity in the polyurethane foam was expected, as thiobencarb possesses a low vapor pressure. Thin-layer chromatography of the foam extracts showed the presence of the parent compound only.

Based on thin-layer chromatography (Table 3) and autoradiography, the products of degradation in water, soil and foam samples were identified. In water, 4-chlorobenzyl alcohol was intermittently detected in all three types of soils, while the parent thiobencarb was identified in all water samples. Desethylthiobencarb was

Table 3. Thin-layer chromatography of thiobencarb and some of its degradation products

Compound	Rf ^a
4-Chlorobenzyl alcohol	0.24
4-Chlorobenzoic acid	0.31
Desethylthiobencarb	0.38
Thiobencarb	0.56

^aSolvent system: Chloroform-diisopropyl ether-n-hexane-acetic acid (10:10:10:1)

found only at 22 days, while 4-chlorobenzoic acid was detected only at 35 days in the water covering the San Joaquin loam.

Few products were detected in the soil samples (Table 4). Apart from the parent compound, 4-chlorobenzoic acid was found in the Willows clay soil 10 days after treatment. In San Joaquin soil, 4-chlorobenzyl alcohol and desethylthiobencarb were detected at 10 and 22 days respectively. Desethylthiobencarb also was detected in Stockton Adobe soil at 22 days, although other workers have

Table 4. Degradation products identified at various intervals after treatment

Soil type	Matrix	Products identified at days after treatment				
		0	10	22	35	45
Willows clay	Water	IV	I, IV	III, IV	I, IV	I, IV
	Soil	IV	II, IV	IV	IV	IV
	Foam	nd	nd	IV	IV	IV
San Joaquin loam	Water	IV	I, IV	I, III, IV	II, IV	I, IV
	Soil	IV	I, IV	III, IV	IV	IV
	Foam	nd	nd	IV	IV	IV
Stockton Adobe clay	Water	IV	I, IV	III, IV	I, IV	I, IV
	Soil	IV	IV	III, IV	IV	IV
	Foam	nd	nd	IV	IV	IV

I = 4-chlorobenzyl alcohol

II = 4-chlorobenzoic acid

III = desethylthiobencarb

IV = thiobencarb

nd = not detected

reported relatively more of the degradation products from their laboratory studies (Ishikawa et al. 1976). The difference could lie in the different types of soils.

Dechlorinated thiobencarb, whose chromatographic properties are similar to those of thiobencarb, was not observed in any of the soil types, even when the soils were augmented with rice straw. It has been reported that amending soil with straw induces the formation of this compound (Moon and Kuwatsuka 1984), but the phenomenon was not observed in our study.

References

- Braverman, M. P., Dusky, J. A. and Locascio, S. J. (1990). Sorption and degradation of thiobencarb in three Florida soils. *Weed Sci.* **38**: 583–8
- Ishikawa, K., Nakamura, Y. and Kuwatsuka, S. (1976). *J. Pesticide Sci.* **1**: 49–57
- Ishikawa, K., Shinohara, R., Yagi, A., Shigematsu, S. and Kimura, I. (1980). Identification of S-benzyl N-N diethylthiocarbamate in paddy field soil applied with benthicarb herbicide. *J. Pesticide Sci.* **5**: 107–9
- Marvel, J. T., Brightwell, B. B., Malik, J. M., Sutherland, M. L. and Rueppel, M. L. (1978). A simple apparatus and quantitative method for determining the persistence of pesticides in soil. *J. Agr. Food Chem.* **26**: 1116–20
- Moon, Y. H. and Kuwatsuka, S. (1984). Properties and conditions of soils causing the dechlorination of the herbicide benthicarb (thiobencarb) in flooded soils. *J. Pesticide Sci.* **9**: 745–54
- Ross, L. J. and Sava, R. J. (1986.) Fate of thiobencarb and molinate in rice fields. *J. Environ. Qual.* **15**: 220–5
- Yusa, Y. and Ishikawa, K. (1977). Disappearance of benthicarb herbicide in irrigation water. *Proc. Asian Pac. Weed Sci. Soc. Conf. 6th* **2**: 596–602