108401

6-11-80

# FILE COPY

Date Out EFB: JUN 11 1980

To: Product Manager 23 Garner
TS-767

From: Dr. Willa Garner
Chief, Review Section No. 1
Environmental Fate Branch

Attached please find the environmental fate review of:

Reg./File No.: 239-EULN, EUUO

Chemical Thiobencarb

Type Product: Herbicide

Product Name: Bolero 8EC, Bolero 10G

Company Name: Chevron

Submission Purpose: Registration on rice

ZBB Code:

ACTION CODE: 162 and 162

Date in: 01/23/80

EFB # 369 and 370

Date Completed: JUN 11 1980

Deferrals To:

- ______ Ecological Effects Branch
- ______ Residue Chemistry Branch
- ______ Toxicology Branch

(1)

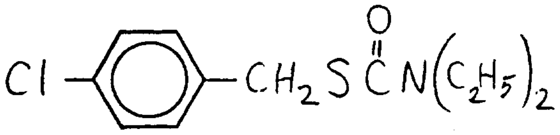
## 1. INDRODUCTION

1.1 This is a request for the registration of the use of thiobencarb on rice. Two formulations of the active ingredient are involved and are designated by the product names Bolero 8EC and Bolero 10G.

1.2 This is a resubmission for this use since our file contains a review of 239-EULN, EUUO dated April 22, 1976. In that review, we concurred with the proposed use.

1.3 The additional data sent in with this resubmission was reviewed for 6(a)(2) purposes.

1.4 Structure and chemical name



S-[(4-chlorophenyl)methyl]diethylcarbamothioate

## 2. DIRECTIONS FOR USE

2.1 See our review of 239-EUUO, EULN dated April 22, 1976.

2.2 With regard to the labels included with this resubmission, the 8EC contains a 6 month rotational crop restriction but the 10G does not.

## 3. DISCUSSION OF DATA

3.1 Benthiocarb: Studies on Residue Level and Behavior in Selected Irrigation Creeks in Agricultural Areas in Saga Pref., Southwestern Japan. Ishikawa, K., T. Oishi and K. Kojima. Kumiai Chemical Industry Co., Ltd. Section of Residue Analysis, Toxicological Laboratory, Life Science Research Institute. March, 1975. Acc. #241476, Tab 2.2.

## Procedure

Ten sampling stations in a rice cultivation area of Saga Prefecture, Kyushu, Southwestern Japan were established for analysis of benthiocarb residues in creek water (Fig. 1) from March through November, 1974. The study covered 80 hectares of rice fields in the Kawazoe-cho district, with an estimated water volume in the creeks under study of 80-90 metric tons. Creeks serve as storage areas for irrigation water until May, when water is pumped from the creeks into rice fields. Creeks resemble large ponds during the storage period.

Station No. 1 was at the upper-most stream of the main waterway, and Station No. 2 was located at the upper-most point of the big creek where the volume of flowing water was maximum (water flows were not quantified). Stations 6, 7, and 8 were located at the western-most, center, and eastern-most points, respectively, on the creek connecting East and West of Fuktomi district. Station 9 was located at the southern-most point of this creek, and Station 10 was located at the end of the irrigation waterway, the final outlet of irrigation water to the Hayatsue River (see Fig. 1 for the location of these and other sampling stations). Irrigation water is introduced to the study area through three channels; the main irrigation waterway (A in Fig. 1); from the big creek (B in Fig. 1) and from the big creek running east of the study area (C in Fig. 1). Irrigation water flows through Stations No. 5, 7, and 9, discharging into the Hayatsue River at Station No. 10.

Water samples from each of the 10 stations were taken 14 times from March 4 through November 29, 1974. One liter samples were collected 50 cm below the surface at each station. Benthiocarb (source and purity not specified) treatment in the study area occurred primarily (quantitative data not provided) from June 28 through July 2. Application was 7% granules at a rate equivalent to 30 kg/hectare in paddy fields flooded with 5 cm water.

## Methodology

Benthiocarb in water was determined by gas chromatography equipped with electron capture detectors, after extraction with dichloromethane. Recoveries of benthiocarb from water ranged from 98.1 to 98.7% with a level of detectability of 0.05 ppb.

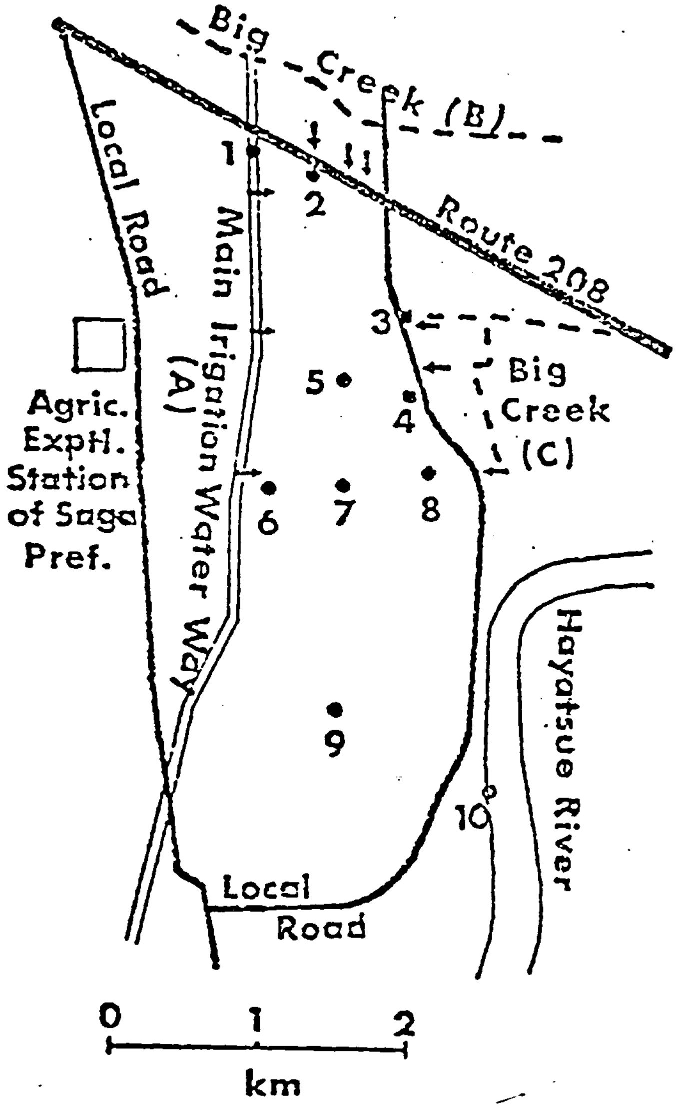


Figure 1. Sampling station is Saga County, Saga Prefecture, Kyushu, Southwestern Japan

Results

Benthiocarb residues in water collected at the 10 sampling stations from March 4 through November 29, 1974 are presented in Table 1. Maximum residues (0.04 ppm, Station 3) were found on July 1, which correlated with benthiocarb treatment in the study area from June 28 through July 2.

Dissipation rate constants and half-lives of benthiocarb in water were calculated, using the July 1st levels as the starting concentration, and ending with levels found on September 9. These results are presented in Table 2, and show an average half-life of 8.8 days.

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Table 1. Benthiocarb concentration in water collected at the sampling stations in agrucultural areas in Saga Prefecture, Southwestern Japan

| Station # | Residue in Water (ppm) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mar. 4 | Apr. 22 | June 3 | June 24 | July 1 | July 8 | July 15 | July 22 | July 29 | August 5 | August 12 | August 19 | Sept. 9 | Nov. 29 |
| 1 | n.d. | n.d. | n.d. | 0.00075 | 0.00166 | 0.00710 | 0.00188 | 0.00018 | 0.00064 | 0.00006 | - | n.d. | n.d. | 0.00009 |
| 2 | 0.00010 | 0.00006 | 0.00007 | 0.00228 | 0.00900 | 0.01400 | 0.00340 | 0.00078 | 0.00051 | 0.00024 | 0.00021 | 0.00025 | n.d. | 0.00018 |
| 3 | - | 0.00006 | - | - | 0.04050 | 0.01440 | 0.00510 | 0.00330 | 0.00205 | 0.00097 | 0.00050 | 0.00071 | 0.00013 | - |
| 4 | 0.00019 | 0.00008 | 0.00011 | 0.00130 | 0.03200 | 0.01620 | 0.00640 | 0.00370 | 0.00164 | 0.00092 | n.d. | 0.00088 | 0.00014 | 0.00018 |
| 5 | 0.00016 | 0.00005 | 0.00008 | 0.00132 | 0.02650 | 0.01800 | 0.00735 | 0.00401 | 0.00162 | 0.00107 | 0.00064 | 0.00035 | 0.00005 | 0.00020 |
| 6 | 0.00011 | n.d. | 0.00011 | 0.00132 | 0.03780 | 0.00800 | 0.00402 | 0.00220 | 0.00220 | 0.00108 | 0.00079 | 0.00078 | 0.00009 | 0.00012 |
| 7 | 0.00013 | 0.00006 | 0.00009 | 0.00103 | 0.03150 | 0.01860 | 0.00730 | 0.00385 | 0.00168 | 0.00115 | 0.00084 | 0.00097 | 0.00007 | 0.00010 |
| 8 | 0.00012 | 0.00007 | 0.00012 | 0.00130 | 0.02500 | 0.0830 | 0.00700 | 0.00360 | 0.00144 | 0.00107 | 0.00069 | 0.00078 | 0.00009 | 0.00012 |
| 9 | 0.00012 | 0.00006 | 0.00019 | 0.00117 | 0.00810 | 0.01860 | 0.00800 | 0.00450 | 0.00198 | 0.00110 | 0.00160 | 0.00100 | 0.00006 | 0.00016 |
| 10 | 0.00020 | 0.00007 | 0.00010 | 0.00100 | 0.02150 | 0.00579 | 0.01030 | 0.00148 | 0.00285 | 0.00080 | 0.00160 | 0.00053 | n.d. | 0.00025 |

Table 2. Rate constants & half-life periods of benthiocarb dissipation from July 1st through September 9th at 10 sampling stations.

| Station # | Rate constant (K) | Half-life period (day) |
|---|---|---|
| 1 | 0.1068 | 6.5 |
| 2 | 0.0926 | 7.5 |
| 3 | 0.0780 | 8.9 |
| 4 | 0.0742 | 9.3 |
| 5 | 0.0860 | 8.1 |
| 6 | 0.0836 | 8.3 |
| 7 | 0.0822 | 8.4 |
| 8 | 0.0793 | 8.7 |
| 9 | 0.0717 | 9.7 |
| 10 | 0.0551 | 12.6 |

## Conclusions

Benthiocarb residues in creek water decline rapidly (average half-life of 8 days) following application of benthiocarb (7% granules, 30 kg/hectare in rice paddy fields) in the rice culture study area. Data are not sufficient to determine the relative importance of dilution versus biological or physico-chemical degradation in the disappearance of benthiocarb. Flow rates in the creek, and between the creek and the surrounding rice paddies, were not provided. Similarly, rainfall and other meteorological data over the study period were not reported.

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3.2 Final Report of Field Study: Ortho Bolero 8EC - Rice, 1979, Brazonia County, Texas, Lauck, J.E., Chevron Chemical Co. Ortho Division, Acc. #241476, Tab 2.3.

## Procedures/Methodology

The distribution and persistence of thiobencarb residues (thiobencarb and its degradation products) were monitored in estuarine environments adjacent to rice fields treated with Bolero 8EC (8 lbs active ingredient per gallon at 4 lb ai/A). The study area involved 35 fields totaling approximately 1987 acres associated with four bayous (Halls Bayou, Pleasant Bayou, Chocolate Bayou, and New Bayou [Figure 1]). Halls Bayou, selected as the principal study site, contained three study areas consisting of 19 fields. One large field in each area was scheduled for treatment with Bolero on the same date. The fields were then scheduled for a synchronized release of flushwater from a controlled flush within two weeks after the application of Bolero. A special study field with direct drainage to the Halls Bayou was selected for a continuous monitor of thiobencarb residue levels in the flushwater during a normal flushing and drainage sequence through the field and into the bayou.

Samples of flushwater were collected at the field outlets from as many of the treated fields as possible in all study areas during each scheduled or rainfall flush. Two-pint composite samples were used for the determination of thiobencarb residue levels. Representative water samples also were collected on a regular basis from collective drainage ditches. Representative composite quart samples were collected by boat at both horizontal and vertical positions from the bayou discharge sites and the bayou.

The sampling sites and associated field designations established for the study are presented in Table 1. Analytical method RM-16 was used to analyze water samples for the determination of thiobencarb residue levels.

Soil samples of ricefield, drainage ditch, and bayou bottom were collected for analysis of thiobencarb residues. A weekly monitor of thiobencarb residue levels in bayou bottom soil also was conducted from collection at upstream and downstream locations from the major field discharge sites for each study area (Area I, II, and III) of Halls Bayou.

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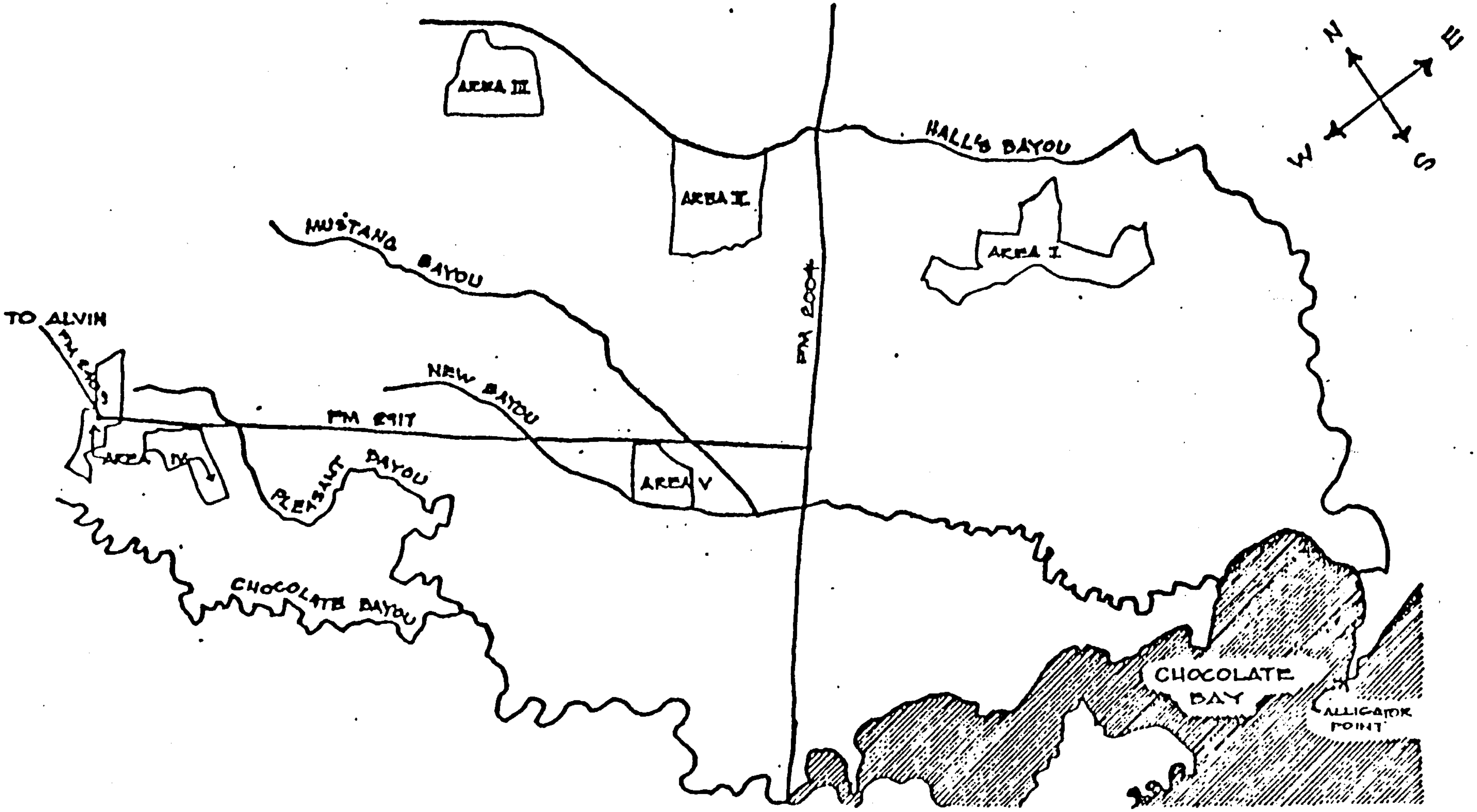

Figure 1. Chocolate Bay Watershed.

Table 1. Description of sampling sites for collections of water, soil, and vegetation.

| Sample site | Description |
|---|---|
| A | Locations where delivery water enters the ricefield inlets during a controlled flush. |
| B | Location where excess water exits the ricefield outlets from a controlled flush or a rainfall flush. |
| C | The collective exit ditch for excess flushwater from the field outlets which flows to the bayou. |
| D | The discharge site where the collective flushwater in the exit ditch enters the bayou. |
| E | The collection location in the bayou 500' upstream (unless otherwise indicated) from the collective flushwater discharge site. |
| F, $F_1$ | The collection location in the bayou 500' downstream (unless otherwise indicated) from the collective flushwater discharge site. |
| $F_1$ (Halls Bayou) | The collection location in Halls Bayou 0.9 miles downstream from Area II where FM 2005 crosses the bayou (Figure 5). |
| $F_1$ (Pleasant Bayou) | The collection location in Pleasant Bayou 800 feet downstream from the confluence of the east and west forks of Pleasant Bayou (Figure 6). |
| $F_2$ (Pleasant Bayou) | The collection location in Pleasant Bayou 2.4 miles downstream from $F_1$ and 500 feet downstream from the discharge site from Pleasant $IV_2$. (Figure 6). |
| $F_3$ (Pleasant Bayou) | The collection location in Pleasant Bayou 1500 feet upstream from the confluence of Pleasant Bayou with Chocolate Bayou |
| $F_4$ (Pleasant Bayou)<br>$F_1$ (Chocolate Bayou) | The collection location in Chocolate Bayou 1500 feet downstream from the confluence of Pleasant Bayou with Chocolate Bayou (Figures 6 and 7, respectively). |

Soil samples were collected prior to application and at various intervals after application and flushing from three locations in the special study ricefield (B-105). From each location, five soil cores (6" in depth by 3" in diameter) were removed at 15-foot intervals. The cores were then sectioned into three parts (upper 1.5", 1.5-3", and 3-6"). The soil from each level of three cores was combined and stored until analyzed. Drainage ditch and bayou soil of Halls Bayou (Area I) was collected at similar intervals with an Ekman grab. Three samples (6" square by 4" in depth) were removed at random from the 1.3 miles of drainage ditch (C) to the bayou from field B-105. The samples were combined, mixed, and a 1-quart composite sample was removed for analysis of thiobencarb residue levels. Similar samples were prepared from collections at the bayou discharge site (D) of area I. The three collections of bottom soil from the bayou (E, F) were removed near each shoreline and in the center to prepare the composite sample. The amount of thiobencarb residues adsorbed by untreated ricefield soil from desorption in flushwater was determined. An untreated area (12' x 12') of B-105 was tarped during application of Bolero 8EC. After flushing the soil, core samples from this area and one core sample from treated area were collected for analysis.

The abundance and diversity of planktos, bayou benthos were determined during the flushing periods after application of Bolero. Thiobencarb residue levels in resident fish, shrimp, and other nektos were determined for seine collections at the two downstream study areas I and II and from trawl collections at study area I of Halls Bayou. The thiobencarb residue level was determined in a hatchery cultured specimen of Halls Bayou indigenous fish (channel catfish, bullhead minnow, striped mullet, and black drum) and grass shrimp caged in bayou water upstream and downstream from a major drainage discharge site at the two downstream study areas (I and II). Analytical method RM 16A-3F was used for determination of thiobencarb residue levels.

Nontarget submerged and emerged aquatic vegetation was collected from the field, the B-105 drainage system, and in Halls Bayou for determination of thiobencarb residue levels.

Downwind nontarget vegetation was also collected at various intervals after application for determination of thiobencarb residue levels from airborne drift. Collection stations were established in a fallow field at 12.5, 25, 50, 100, 200, and 400 meters downwind from the special study ricefield. A rush (*Juncus sp.*), a nutgrass (*Cyperus sp.*), and hedge parsley (*Torilis nodosa*) were collected for analysis as representative grassy and broadleaf plants. This study was intended to complement the special drift studies. The vegetation samples were harvested by hand, wrapped in aluminum foil and paper bags, and stored in a freezer until analysis.

Emerged levee vegetation adjacent to a study field (Pleasant $IV_2$, A-23) was covered in four locations with black plastic tarps prior to application. Four similar areas were left uncovered. The tarps were removed after application and the treated and untreated vegetation was rated for injury after 17 days. Similarly, predominant bayou trees and shrubs immediately bordering a study field (i.e. within 15 feet; Halls Bayou II, B-11) were examined for injury. Four terminals were covered with paper bags on four trees or shrubs of each species. The treated and untreated terminals were rated for injury 18 days after application.

The actual level of airborn drift from Bolero was examined. The position of nozzle discharge relative to the airstream also was adjusted to vary the potential for airborne drift. The deposits from a single swath applied by air were collected on filter paper and analyzed for thiobencarb residue levels. Filter paper sheets (Whatman #1, 6" x 21.5") stapled to particle board were placed in the study fields in downwind locations at distances 12, 25, 50, 100, 200, and 400 meters from the center of the swath. Upwind stations were established at 12, 25, and 50 meters from the center of the swath. A collection station was also established at the center of the swath. For the second study collection stations were added 500 and 700 meters downwind and 100 meters upwind. Collection stations were added 800 and 1,200 meters downwind and 50 meters upwind for the third study. Bolero 8EC was applied at the suggested label rate in a single swath perpendicular to the wind direction and collection surfaces. The papers were collected 10 minutes after application, placed in quart jars with 10 ml distilled water, and capped. Additional information on analysis was not available.

## Results

### a. Water

Some 71 residual water samples were collected at the outlets of 28 fields throughout the flushing period representing drainage from the four bayous (Tables 2-4). Controlled flushes were normally scheduled within 7-10 days after application with corresponding residual water entering the bayou 1-5 days later. The rainfall flushes were observed within a few hours to several days after application. The level of thiobencarb residues in flushwater generally conformed to the expected desorption curve, which was calculated from the actual recovery figures of 28 fields (Figure 2). An average thiobencarb level of 1.5 ppm was found in flushwater 1 day after application and 0.2 ppm (from 9 fields) was observed 2 days after application. Flushwater from rainfall flushes collected at the field outlets contained higher levels of thiobencarb than observed for scheduled flushes. For example, thiobencarb residue levels of 8.9 ppm were recorded from field B-12 in flushwater resulting from a heavy rainfall (3.23 inches) within hours of application.

Progressively lower levels of thiobencarb residues were recovered from drainage ditchwater as the distance from the field outlet toward the bayou increased. The decrease of the thiobencarb residual level observed in transport to the bayou was most notable during rainfall flushes. Thiobencarb recovery data from drainages of three separate fields demonstrated a series of dilutions from the field outlet to each consecutive downstream sampling site. The thiobencarb residue level of 0.164 ppm at the field outlet (B) of field A-22 (Area IV, Pleasant Bayou) was diluted to 0.016 ppm at C (1,700 feet from B), to 0.010 ppm at location C (1,700 feet from C, and 1,700 feet from D), to 0.008 ppm at the drainage discharge site (D), and to the limit of detection, 0.002 ppm, in the bayou after 24 hours of rainfall run-off. Similarly, thiobencarb residue levels at the field outlets of field C-1 (Area I, Halls Bayou) and field B-12 (Area II, Halls Bayou), recorded at 0.595 ppm and 8.9 ppm, were diluted to 0.28 and 0.69 ppm, respectively, at the corresponding drainage discharge sites to the bayou. Residual water from scheduled flushes was also diluted in transport by drainage ditch to the bayou. Residue levels recovered in flushwater collected from the drainage of field B-105 initiated 13 days after application were 0.12 ppm at the field outlets, 0.06 ppm, 0.004 ppm, and 0.006 ppm at drainage discharge site (D), bayou location E, and F', respectively, 12 hours after overflow initiation.

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Table 2. Thiobencarb residues in flushwater, drainage water, and bayou water collected from Hallo Bayou (Areas I, II, and III)

| | Thiobencarb residues (ppm) in water samples from sample site | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | B | | | | | | | | | | | | C | | D | | | E | F' | F | E | F | E | F |
| Date | B-105 | B-56 | C-1 | C-14 | C-15 | B-12 | B-13 | B-14 | B-15 | B-16 | A-109 | A-110 | $B_{12}$ | C-1, B-96 | R-105 | R-12 | C-1, R-96 | Area I | | | II | | III | |
| 3/20 | | — app — | | | | | | | | | | | | | | | | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.003 |
| 21 | | | | | | | | | | | | | | | | | | 0.000 | 0.000 | | | | | |
| •22 | | U.F.<br>0.142 | 0.59 | | | | | | | | | | | 0.280 | | | .282 : | .000 | .011 | | | | | |
| •23 | | | 0.315 | | | | | | | | | | | | | | | .000 | .000 | | | | | |
| •24 | | | | | | | | app<br>3.4 | | | | | | | | B-13, 14, 15, 16<br>0.140 | | .000 | .000 | | | | | |
| •25 | app. | | | | | | | | | | app | | | | | | | .002 | .002 | | .016 | .026 | | |
| 26 | | | | | | | | | | | | | | | | | | .002 | .002 | | .002 | .003 | - | - |
| 27 | | | | | | | | | | | | | | | | | | | | | | | .000 | <.002 |
| 28 | | | | | | | | | | | | | | | | | | | | .000 | | .004 | | |
| 4/•1 | | | | | | | | | | | | | | | | | | | | | - | - | | |
| •2 | | | | | | | | | | | | | | | | | | | | | | | | |
| •3 | S.F. | | | | | | | | | | | S.F.<br>.393 | | | | | | .001 | .000 | | | | | |
| •4 | | | | | | | - | - | - | S.F.<br>.16 | | | | | | | | - | - | <.002 | - | <.002 | .000 | .019 |
| 5 | | | | | | | S.F.<br>.203 | - | S.F.<br>.021 | .14 | | | | | | | | .002 | — | <.002 | .041 | <.033 | .011 | .012 |
| 6 | | | S.F.<br>.027 | | | | | - | .179 | - | | | | | | | | .002 | <.002 | .003 | .048 | .040 | .164 | .000 |
| 7 | 0.109 | | | | | | | S.F.<br>.253 | .177 | - | S.F.<br>.405 | | | | .037 | | | .04 | .015 | .003 | .083 | .064 | .007 | .140 |
| •8 | 0.123 | | | | | | | | | | | | | | .067 | | | .031 | .027 | .008 | | .033 | .003 | .004 |
| 9 | 0.081 | | | | | | | | | | | | | | .034 | | | .004 | .003 | .003 | | .010 | <.002 | .002 |
| 10 | | | | | | | | | | | | | | | | | | | | .003 | | .010 | .000 | .000 |
| •11 | | | | | | | | | | | | | | | .009 | | | .009 | 0.11 | .002 | | .014 | .003 | <.002 |
| 12 | | | | | | | | | | | | | | | | | | | | .010 | | .021 | .000 | .000 |
| 13 | | | | app | | | | | | | | | | | | | | | | | | | | |
| 14 | | | | | | | | | | | | | | | | | | | | | | | | |
| 15 | | | | | | | | | | | | | | | .013 | | | .014 | .008 | - | | | | |
| •16 | | | | | | | | | | | | | | | | | | | | | | | - | - |
| •17 | | | | | | | | | | | | | | | | | | | | .003 | | .008 | .002 | .000 |
| •18 | | | | | | | | | | | | | | | | | | | | | | | | |
| •19 | | | | U.F.<br>- | 0.006 | app<br>8.9 | U.F. | | | | | | 0.94 | - | | .69 | | | | | | | | |
| •20 | 0.000 | .005 | .007 | .091 | .097 | 0.3 | - | - | - | - | U.F.<br>.028 | - | 0.33 | - | .007 | .31 | | .006 | .006 | .005 | .002 | .002 | | |
| •21 | 0.000 | | | | | 0.4 | .039 | .031 | .024 | | | | 0.13 | | | .13 | | | | | .003 | .003 | - | - |
| •22 | | | | | | | | | | | | | | | | | | | | | | | .000 | .003 |
| 24 | | | | | | | | | | | | | | | | | | | | .003 | - | .000 | .000 | .003 |
| 29 | P.F.<br>0.014 | | | | | | | | | | | | | | .005 | | | .000 | .000 | | | | | |
| •30 | | | | | | | | | | | | | | | | | | | | | | .004 | .000 | <.002 |
| 5/01 | | | | | | | | | | | | | | | | | | | | .002 | | | | |
| 6 | .007 | | | | | | | | | | | | | | .003 | | | .003 | .003 | | | | | |

• Rainfall
app - Applied Bolero
U.F. - Unscheduled flush
S.F. - Scheduled flush
P.F. - Permanent flood

Table 3. Thiobencarb residues in flushwater and bayou water collected from Pleasant Bayou (Area IV).

| | B | | | | | | | | | Bayou sampling sites | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Area $IV_1$ | | Area $IV_2$ | | | | Area $IV_3$ | | | | | | |
| Date | A-13 | A-108 | A-9 | A-10 | A-11 | A-19 | A-23 | A-24 | A-25 | $F_1$ | $F_2$ | $F_3$ | $F_4$ |
| 3/14 | app | | | | | | | | | | | .000 | .000 |
| 3/20 | | app | | | | | | | | | | | |
| 21 | U.F.<br>.100 | 1.39 | | | | | | | | | | | |
| *22 | .105 | 0.710 | | | | | | | | 0.41<br>0.400 | | 0.002<br>0.035 | 0.000.<br>0.003 |
| *23 | | | | | | | | | | | | | |
| *24 | | | | | | | | | | | | | |
| *25 | | | | | | | | | | - | | 0.003 | - |
| 3/29 | S.F.<br>.071 | S.F.<br>- | | | | | | | | | | | |
| 4/*2 | | | | | | | | | | 0.051<br>0.087 | | 0.002 | 0.000 |
| *3 | | .109 | | | | | | | | | | | |
| *4 | | | | | | | | | | | | | |
| 4/*8 | | | | | | | ├── app ──┤ | | | | | | |
| 9 | | | | | | | - | S.F.<br>- | S.F.<br>0.193 | | | | |
| 10 | | | | | | | - | - | - | | | | |
| *11 | | | | | | | - | | .320 | | | | |
| 12 | | | | | | | - | | | | | | |
| 13 | | | | | | | - | | | | | | |
| 14 | ├─ P.F. ─┤ | | | | | | - | S.F. | | | | | |
| 15 | | | | | | | - | .071 | - | | | | |
| *16 | | | ├──── app ────┤ | | | | S.F. | | | - | - | - | - |
| 17 | | | U.F. | | | | | | | | | | |
| *18 | | | 1.470 | - | - | - | .061 | | | - | 0.003 | 0.002 | 0.003 |
| *19 | U.F.<br>.053 | | | | U.F. | | ├── U.F. ──┤ | | | | | | |
| *20 | | | 0.181<br>.041 | .186<br>- | .203<br>.073 | .197<br>- | - | - | - | 0.052<br>0.015 | 0.005<br>0.008 | 0.003<br>0.003 | 0.000<br>0.000 |
| *21 | .012 | | .070 | .091 | .134 | - | | .038 | | 0.034 | 0.015 | 0.000 | 0.000 |
| *22 | | | | | | | | | | | | 0.011 | 0.005 |
| 4/*30 | .010 | | ├──── U.F. ────┤ | | | | | | | | | | |
| 5/01 | | | .005 | .063 | .060 | .069 | 0.30 | - | - | 0.007<br>0.028 | 0.005<br>0.005 | 0.006<br>0.000 | 0.002<br>0.000 |

* - Rainfall.

app - Applied Bolero.

U.F. - Unscheduled flush.

S.F. - Scheduled flush

P.F. - Permanent flood.

B - Field outlets.

$F_1$, $F_2$, $F_3$, $F_4$ - Refer to Table 1.

able 4. Thiobencarb residues in flushwater, drainage water, and bayou water collected from Chocolate Bayou and New Bayou (Area $IV_2$, $IV_3$, Area V).

| | Thiobencarb residues (ppm) in water samples from sample site | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Area $IV_3$ | Area $IV_2$ | | Area V | | | | | Chocolate Bayou | | | New Bayou | | | |
| Date | A-12 | A-14 | A-22 | B-152 | B-153 | $C_1$ | $C_2$ | D(A-22) | E | F | $F_1$ | E | F | $F_1$ | $F_2$ |
| *3/24 | | | | | | | | | | | | 0.000 | 0.000 | | |
| * 25 | | | | — App. — | | | | | | | | - | - | .003 | .002 |
| *4/1 | | | | | | | | | | | | - | - | .003 | .002 |
| *4/3 | | | | .027 | .287 | | | | | | | <.001 | .068 | .064 | .022 |
| 5 | | | | | | | | | | | | | | | |
| 6 | | | | | | | | | | | | | | | |
| 7 | | | App. | | | | | | | | | | | | |
| *8 | | | | | | | | | | | | | | | |
| *16 | — App. — | | | | | | | | | | | | | | |
| *17 | - | u.f.<br>2.110 | - | | | | | | 0.000 | 0.000 | | <0.001 | 0.000 | 0.002 | 0.007 |
| *18 | | | | | | | | | | | | | | | |
| *19 | 0.313 | u.f.<br>0.215 | 0.164 | | | .030 | .019 | | | | 0.000 | | | | |
| *20 | | | 0.028 | | | .016 | .010 | .008 | 0.002 | .002 | 0.000 | | | | |
| *21 | | | 0.057 | | | | | | | | 0.000 | | | | |
| *22 | | | | | | | | | | | | | | | |
| *4/30 | 0.05 | u.f.<br>.068 | | | | | | | | | 0.000 | | | | |
| 5/1 | | | | | | | | | | | | | | | |
| 6 | | | | | | | | | | | | | | | |
| 8 | | | | | | | | | | | | | | | |
| 13 | | | | | | | | | | | | | | | |

*Rainfall
APP Applied Bolero
U.F. Unscheduled Flush

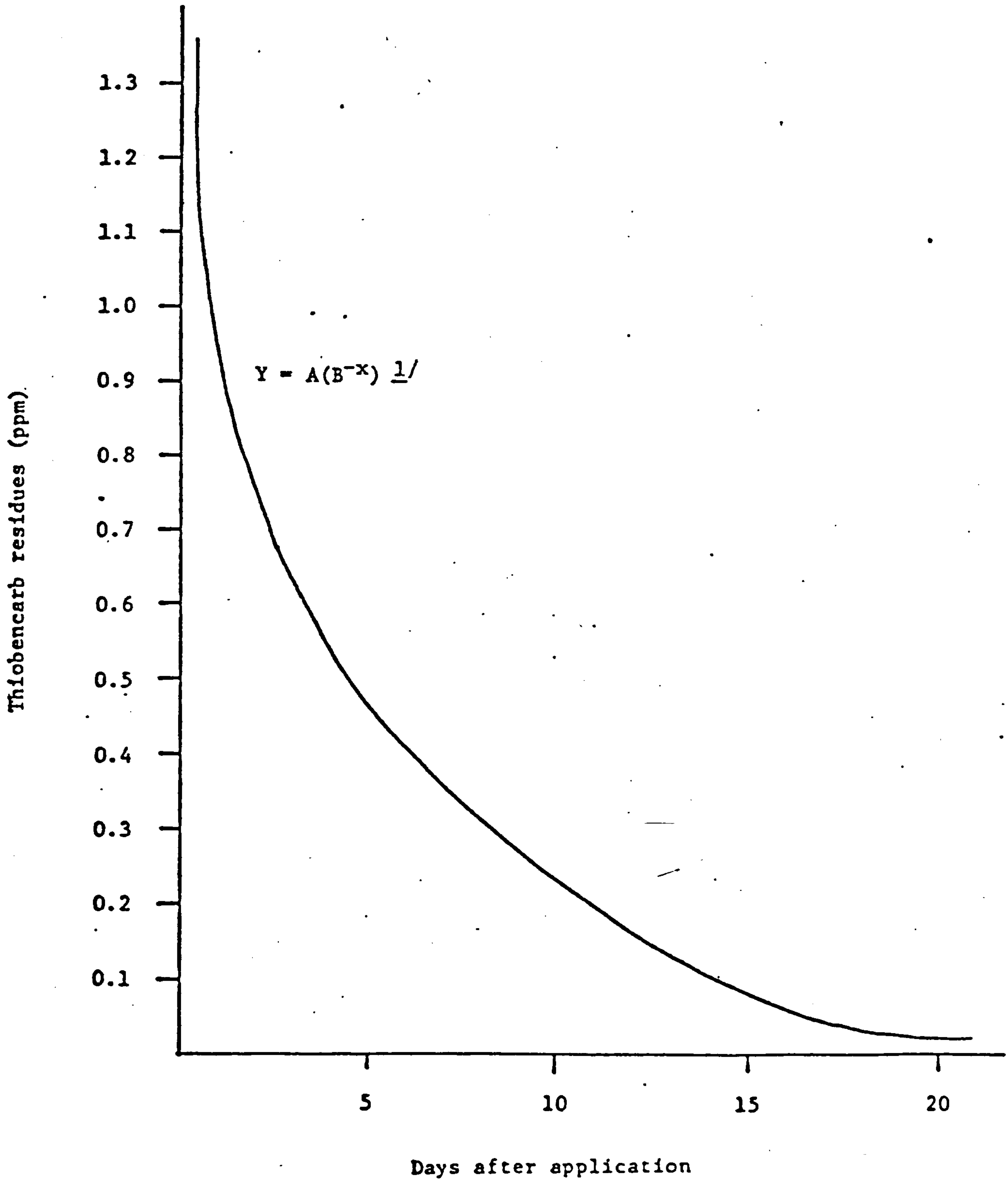

Figure 2. Expected desorption of thiobencarb in flushwater from ricefields treated with BOLERO 8 EC.

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Analysis of bayou water samples collected downstream from each study area of Halls Bayou during the coordinated residual flushwater release from the three study areas (4-7-79) showed the actual dilution of thiobencarb that occurred in the bayou corresponded to the volume of water present in the bayou. At peak overflow, thiobencarb residue levels recovered in bayou water upstream and downstream from the drainage discharge site were both in the range of 0.01-0.04 ppm for Area I, 0.06-0.08 ppm for Area II, and 0.14-0.16 ppm for Area III. All fields were treated within a 3-day period and were flushed simultaneously within two weeks. The bayou water volume at the respective collection sites were 969, 622, and 187 $ft^3$ per foot of bayou length. Thiobencarb levels at the farthest downstream location F of Halls Bayou ranged from 0.002 to 0.003 ppm throughout the study period. Daily monitoring of Halls Bayou water showed that maximum thiobencarb residue levels recovered from each study area persisted for only 24-48 hours, which corresponded to a period of peak drainage of residual flushwater. Thiobencarb at a level of 0.164 ppm was recovered from bayou water (Area III), which was reduced to 0.003 ppm 48 hours later. Similarly, the peak residue levels of bayou water from Area I and II persisted for only 24 hours. Pleasant Bayou water collected downstream from the drainage discharge site of Area $IV_2$ contained thiobencarb residue levels of 0.05 ppm 3 days after application and immediately after an unscheduled rainfall flush. However, thiobencarb at a level of 0.4 ppm was recovered from bayou water 1 day after application followed with a rainfall flush. Thiobencarb residues at levels ranging from nondetectable to 0.003 ppm were recovered from the bayou water collected at the confluence of Pleasant Bayou with Chocolate Bayou throughout the study (weekly monitor data). Thiobencarb at a level of 0.06 ppm was found in New Bayou water samples collected downstream from fields B-152 and B-153 8 days after application, and a residue level of 0.002 ppm was found 12 days later. Thiobencarb at levels of nondetectable to 0.002 ppm were recovered upstream and downstream from Chocolate Bayou water throughout the study.

The volume of water in the bayou was largely influenced by wind, tidal activity, and rainfall. Daily high and low tides in Halls Bayou during the flushing period were predicted to fluctuate roughly between 0-1 feet in the absence of wind. The calculated increase in bayou water volume from an increase of 1 foot from the mean tide level would range from 10-16% at downstream location to 187% at upstream sampling sites.

b. Soil

Essentially no thiobencarb was recovered from bayou bottom soil collected weekly from each study area of Halls Bayou. Recoveries of thiobencarb from ricefield soil samples collected from three locations (check a, b, c) of field B-105 are presented in Table 5. Recoveries at the 0-1.5 inch level ranged from 76-93% of the total recovery (from all sample levels of the three study checks), 4-17% of the total recovery for the 1.5-3" level, and 3-7% of the total recovery for the 3-6" level.

Seven days after flush overflow, thiobencarb residue levels of 0.05 ppm were recovered from soil samples collected at drainage ditch (c) and at bayou sampling site, F'. The thiobencarb residue level of drainage ditch soil increased to 0.12 ppm 17 days after flush overflow, whereas the soil of drainage discharge site (D) contained 0.14 ppm, the maximum recovery found from the drainage access. Thiobencarb readsorbed by untreated ricefield was about 21% (average 0.34 ppm) of the concentration in adjacent treated ricefield soil (1.62 ppm).

c. Bioaccumulation

The resultant data for planktos and bayou benthos were not provided. The residue levels of thiobencarb and its metabolite, 4-chlorobenzyl methyl sulfone, in resident fishes, shrimp, and other nektos (21 species) of seine collections 100 feet up and downstream from the discharge sites (Areas I & II) of Halls Bayou are presented in Tables 6 & 7.

The average thiobencarb residue level in these organisms increased from 0.1 ppm (4 days post application) to 0.9 ppm (13 days post application) and then decreased to 0.3 ppm (28 days post application) in the Halls Bayou (Area I). Correspondingly the residue level of 4-chlorobenzyl methyl sulfone ranged from 0.1 to 0.5 ppm during the same test period. The average residue levels of thiobencarb and 4-chlorobenzyl methyl sulfone in the organisms collected from Halls Bayou (Area II) ranged from 0.2 to 2.6 ppm and 0.3 to 0.8 ppm, respectively, during the 5-30 day post application period. The highest thiobencarb residue level, 4.6 ppm, was found in Mosquito fish 30 days after application, and the highest residue level of 4-chlorobenzyl methyl sulfone was found in Bay anchovy (<1.8 ppm) 19 days after application.

The average thiobencarb residue level of caged species in bayou water (Area I) ranged from 0.1 to 2.2 ppm during the 10-18 day post application period, and the residue level of 4-chlorobenzyl methyl sulfone ranged from 0.02 to 2.2 ppm during the same period. A thiobencarb level of 6.1 ppm was found in the Bullhead minnow 12 days after application which fell to 2.7 ppm 1 day later. The striped mullet also contained thiobencarb at <4.5 ppm and 4-chlorobenzyl methyl sulfone at <6.5 ppm at 14 days after application, which fell to <2.3 ppm and 3.2 ppm, respectively, 1 day later.

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Table 5. Thiobencarb residues in soil collected at three locations in the Special Study Field (B-105) Area I, Halls Bayou 1/.

| | | Thiobencarb residues (ppm) in ricefield soil | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | First check 2/ | | | Middle check | | | Last check | | |
| (1979) | Sample interval (days after application) | 0.0"-1.5" | 1.5"-3.0" | 3.0"-6.0" | 0.0"-1.5" | 1.5"-3.0" | 3.0"-6.0" | 0.0"-1.5" | 1.5"-3.0" | 3.0"-6.0" |
| 3-23 | Pretreatment | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.05 | 0.00 |
| 3-25 | Day of application | 3.6 | 1.2 | 0.23 | 4.20 | 0.41 | 0.27 | 7.7 | 0.69 | 0.79 |
| 3-26 | One day after application | 0.88 | 0.16 | 0.09 | 6.0 | 0.09 | 0.05 | 0.96 | 0.00 | 0.05 |
| 4-1 | One day prior to flush initiation (7) | 0.69 | 0.00 | 0.00 | 4.2 | 0.12 | 0.05 | 6.4 | 0.00 | 0.5 |
| 4-9 | Seven days after flush initiation (15) | 1.0 | 0.07 | 0.00 | 0.25 | 0.03 | 0.05 | 1.6 | 0.07 | 0.05 |
| 4-17 | 15 days after flush initiation (23) | 0.14 | 0.00 | 0.22 | 0.50 | 0.00 | 0.00 | 1.0 | 0.00 | 0.00 |

[1] BOLERO applied 3-25-79.

[2] First check (paddy) to receive flush water..

Table 6. The residue levels of thiobencarb and 4-chlorobenzyl methyl sulfone in non-target aquatic organisms (fish, crabs, shrimp, crawfish) of Halls Bayou by seine collection, Area I. (Field B-104, B-96, C-1) Aerial application 4lb ai/A on 3/20 & 3/25)

| Days after application | Thiobencarb (ppm) | | | | 4-chlorobenzyl methyl sulfone (ppm) | | | |
|---|---|---|---|---|---|---|---|---|
| | 100' upstream | | 100' downstream | | | | | |
| | E | | F | | E | | F | |
| | Range | Mean | Range | Mean | Range | Mean | Range | Mean |
| 4 | <0.03-0.23 | <0.1 | <0.02-0.4 | 0.2 | <0.03-0.31 | 0.1 | <0.05-0.61 | 0.3 |
| 12 | <0.03-3.3 | 0.6 | 0.03-0.56 | 0.2 | <0.03-0.21 | 0.1 | <0.04-0.15 | 0.1 |
| 13 | <0.24-2.0 | 0.9 | <0.34-1.7 | 0.8 | <0.16-<0.84 | 0.5 | 0.09-<0.5 | 0.3 |
| 18 | 0.27-<0.68 | 0.4 | <0.23-0.42 | 0.3 | <0.04-1.1 | 0.4 | <0.04-<0.66 | 0.4 |
| 28 | <0.12-0.35 | 0.2 | <0.07-<0.93 | 0.3 | <0.03-<0.42 | 0.2 | <0.03-1.1 | 0.4 |

Table 7. The residue levels of thiobencarb and 4-chlorobenzyl methyl sulfone in non-target organisms (fish, crab, shrimp) of Halls Bayou by seine collection, Area II (B-13, B-14, B-15, B-16) Aerial application 4 lb ai/A (3/24)/

| Days after application | Thiobencarb (ppm) | | | | 4-chlorobenzyl methyl sulfone (ppm) | | | |
|---|---|---|---|---|---|---|---|---|
| | 100' upstream | | 100' downstream | | | | | |
| | E | | F | | E | | F | |
| | Range | Mean | Range | Mean | Range | Mean | Range | Mean |
| 5 | 0.09-0.47 | 0.2 | 0.01- 0.39 | 0.2 | <0.08-<0.43 | 0.26 | <0.03-<0.52 | 0.28 |
| 13 | - | - | <0.56-2.8 | 1.4 | - | - | <0.04-<0.99 | 0.5 |
| 14 | 0.26-1.6 | 0.9 | 0.04-2.3 | 0.6 | <0.03-<0.04 | 0.04 | <0.03-<1.4 | .3 |
| 19 | <0.3-<1.1 | .8 | .94-4.2 | 2.6 | <0.04-<1.8 | 0.8 | <0.04-<0.57 | .2 |
| 30 | 0.28-4.60 | 1.62 | <0.08-<0.92 | 0.5 | 0.26-1.2 | 0.7 | <0.14-<1.1 | .6 |

The highest thiobencarb residue levels found in clam, grass shrimp, and oysters after application were 1.7 (18 days), 0.46 (12 days), and 0.07 ppm (14 days), respectively, whereas no 4-chlorobenzyl methyl sulfone residues were detected in clams and oysters, and a level of 0.32 ppm was found in grass shrimp. Four aquatic organisms were caged in bayou water (Area II) for the determination of residue levels. The thiobencarb residue level in Bullhead minnow ranged from 0.9 to 3.6 ppm 12-19 days after application. The 4-chlorobenzyl methyl sulfone residue level ranged from <0.05 to 0.3 ppm during the same period. During the 12-19 day post application period, the thiobencarb residue level was 0.7-6.6 ppm in catfish, 0.03-0.5 ppm in grass shrimp, and 1.5 to 13 ppm in striped mullet and the levels of 4-chlorobenzyl methyl sulfone in these testing species ranged from 0.02 to 0.5 ppm. The residue levels in aquatic organisms (atlantic croaker, blue catfish, blue crab, carp, channel catfish, southern flounder, spotted gar, and river shrimp) taken by trawl collection 500 feet up and downstream from the drainage discharge site (Area I) of Halls Bayou were determined. The residue levels of thiobencarb and 4-chlorobenzyl methyl sulfone ranged from <0.03 to 0.6 ppm and <0.04 to 0.4 ppm, respectively, 12 - 28 days after application.

### d. Vegetation

Of all the levee vegetation directly exposed to Bolero by an aerial application, only canarygrass demonstrated symptoms of injury. The size and maturity of affected plants was reduced by 53% relative to untreated plants covered with a trap during application. Tolerant species of non-target vegetation were Bromegrass (*Bromus spp.*) Little Barley (*Hordeum pusillum*), Sunflower (*Helianthus spp.*), Evening Primrose (*Oenothera speciosa*), Spurge (*Euphorbiaceae*), Venus looking glass (*Triodanis perfoliata*), Hedge parsley (*Torolis spp.*), Purple nutsedge (*Cyperus rotundus*), Snakegrass (*Juncus spp.*), Myrtle (*Myrtus communis*), Chinaberry (*Milia azedarack*), and Live oak (*Quercus spp.*).

Non-target submerged and emerged vegetation were collected for determination of thiobencarb residues and its two metabolites, 4-chlorobenzyl methyl sulfone and 4-chlorobenzoic acid. The resultant data are presented in Table 8. The level of thiobencarb residues ranged from nondetectable to 0.2 ppm for submerged vegetation and 0.08 to 0.5 ppm for emerged vegetation. The level of 4-chlorobenzoic acid ranged from nondetectable to 0.02 ppm in all studied vegetation, and no detectable 4-chlorobenzyl methyl sulfone was found in both submerged and emerged vegetation.

Downwind vegetation (broadleaf weed and sedge) adjacent to the treated field (B-105) was collected to determine the levels of thiobencarb and its two metabolites. Three days before treatment, the broadleaf weed contained an average of 0.2 ppm thiobencarb (0.00-0.64 ppm) and 0.01 ppm 4-chlorobenzoic acid; whereas sedge contained 0.2 ppm (0.08-0.76 ppm) and 0.17 ppm (0.01-0.61 ppm), respectively. 4-Chlorobenzyl methyl sulfone in these tested vegetations was nondetectable. The broadleaf weed and sedge were also collected at specific distances from the edge of treated field immediately after application and 7, 14, and 21 days after application. The residue levels of thiobencarb and its two metabolites were determined and are presented in Table 9. In general, the residue levels of thiobencarb and its two metabolites in vegetation samples decreased with increasing distance from the edge of the field. However, the residue levels of thiobencarb in broadleaf weed samples collected 25 meters from the treated field 14 and 21 days after application (4.6 and 5.5 ppm, respectively) are much higher than the levels found in samples collected 12 meters from the field (10.3 and 0.6 ppm, respectively).

### e. Drift

Upwind and downwind thiobencarb drift data are presented in Table 10. Very small amounts of thiobencarb were recovered at upwind or downwind stations 100 meters or more from the center of swath. In study II, virtually no thiobencarb was recovered upwind from the center of swath when horizontal wind speed averaged 7.6 mph. Recoveries at upwind stations increased as the horizontal wind speed decreased in the other two studies.

Table 8. The residue levels of thiobencarb (T), 4-chloro benzyl methyl sulfone (CBMS), and 4-chlorobenzoic acid (CBA) in non-target vegetation.

| Vegetation/location | Days after application | -2* | 15 | 21 | 22 | 32 |
|---|---|---|---|---|---|---|
| | Residues determined | Residue (ppm) | | | | |
| Submerged vegetation F upstream from point of ditch discharge (Halls Bayou) | T | 0.00 | 0.05 | 0.05 | - | 0.08 |
| | CBMS | 0.00 | 0.00 | 0.00 | - | 0.00 |
| | CBA | 0.02 | 0.00 | 0.00 | - | 0.00 |
| Emerged vegetation C-ditch adjacent to Field B-105 | T | 0.34 | 0.52 | 0.08 | - | 0.08 |
| | CBMS | 0.00 | 0.00 | 0.00 | - | 0.00 |
| | CBA | 0.00 | 0.00 | 0.01 | - | 0.02 |
| Submerged vegetation (C-D) ditch adjacent to fields near points of discharge | T | - | 0.20 | 0.11 | 0.12<br>0.07 | 0.20 |
| | CBMS | - | 0.00 | 0.00 | 0.00 | 0.00 |
| | CBA | - | 0.02 | 0.00 | 0.00 | 0.00 |

* pretreatment, 2 days before application.

Table 9. The residue levels of thiobencarb (T), 4-chlorobenzyl methyl sulfone (CBMS), and 4-chlorobenzoic acid (CBA) in non-target vegetation (drift).

| Sample discription | Distance from edge of fields (M) | 12 | 25 | 50 | 100 | 200 | 400 |
|---|---|---|---|---|---|---|---|
| | Residues determined | Residues (ppm) | | | | | |
| Broadleaf weed & sedge (composite) 0 day after application | T | 7.1 | 1.6 | 0.9 | 0.4 | 0.5 | 0.4 |
| | CBMS | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | CBA | 0.3 | 0.01 | 0.03 | 0.02 | 0.02 | 0.01 |
| Broadleaf weed & sedge (composite) 7 days after application | T | 1.4 | 0.08 | 0.08 | 0.09 | 0.1 | 0.05 |
| | CBMS | 0.07 | 0.00 | 0.03 | 0.00 | 0.00 | 0.00 |
| | CBA | 0.12 | 0.00 | 0.00 | 0.18 | 0.03 | 0.07 |
| Sedge 14 days after application | T | 2.3 | 0.15 | 0.14 | 0.12 | 0.12 | 0.01 |
| | CBMS | 0.05 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | CBA | 0.85 | 0.29 | 0.13 | 0.04 | 0.14 | 0.05 |
| Broadleaf weed 14 days after application | T | 0.27 | 4.6 | 4.1 | 0.86 | 0.62 | 0.56 |
| | CBMS | 0.03 | 0.04 | 0.00 | 0.00 | 0.00 | 0.00 |
| | CBA | 0.16 | 0.05 | - | 0.05 | 0.02 | 0.02 |
| Sedge 21 days after application | T | 1.0 | 0.08 | 0.13 | 0.58 | 0.10 | 0.06 |
| | CBMS | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | CBA | 0.58 | 0.13 | 0.13 | 0.04 | 0.08 | 0.03 |
| Broadleaf weed 21 days after application | T | 0.62 | 5.5 | 1.3 | 0.58 | 0.52 | 0.33 |
| | CBMS | 0.05 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | CBA | 0.77 | - | 0.03 | 0.04 | 0.02 | 0.01 |

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Table 10. Thiobencarb deposits from fallout and variables associated with the studies.

| Location of collection papers -- (meters) | | Average thiobencarb deposits (ug) | | |
|---|---|---|---|---|
| Upwind | Downwind | I | II | III |
| 100 | | --- | 0 | --- |
| 50 | | 11 | 0 | 11 |
| 25 | | 3 | 0 | 8 |
| 12 | | 6 | 1 | 11 |
| center of swath | | --- | --- | 6449 |
| | 12 | 2113 | 2613 | 5556 |
| | 25 | 930 | 849 | 786 |
| | 50 | 164 | 549 | 168 |
| | 100 | 79 | 106 | 27 |
| | 200 | 119 | 20 | 11 |
| | 400 | 19 | 6 | 7 |
| | 500 | --- | 3 | --- |
| | 700 | --- | 21 | --- |
| | 800 | --- | --- | 5 |
| | 1200 | --- | --- | 4 |

| Variable | I | II | III |
|---|---|---|---|
| Positions of nozzles to airstream | 0°(back) | 90°(down) | 90°(down) |
| Mean wind speed (mph 16) | 0.43 | 7.63 | 5.9 |

Limit of detection 1.5 mg. Deposits recovered per 825 $cm^2$

## Conclusions

Ricefields (approximately 2000 acres) associated with four bayous at Brazonia County, Texas were treated with Bolero (8EC) via aerial application at a rate of 4 lb ai/A. The thiobencarb residues dissipate fairly rapidly in soil and water. Only negligible residues remained in either soil or water 20 days after application. On the day of application, the average thiobencarb residue level of 6 ppm was found in soil, and an average level of 1.3 ppm was found in flushwater collected at outlets of ricefields. Two weeks after application, the residue level in soil was 0.35 ppm or 94% reduction and in flushwater was 0.12 ppm or 91% reduction.

The residue level in flushwater at the field outlets is altered by considerable dilution during transport to the bayou via the drainage ditches. Standing ditchwater and residual water from other fields (fallow fields, open land) associated with the same drainage system constitute the major sources for dilution. The thiobencarb residue concentration in flushwater was further diluted in the bayou. The actual degree of dilution correspond with the volume of water present in the bayou. The volume of water in the bayou was notably influenced by wind, tidal activity and rainfall. Thiobencarb residue levels in bayou water fluctuated with tidal activity. During the period of study, the thiobencarb residue level in bayou water ranged from 0.00 to 0.16 ppm for Halls Bayou, 0.00 to 0.40 ppm for Pleasant Bayou, 0.00 to 0.07 ppm for New Bayou, and 0.00 to 0.002 ppm for Chocolate Bayou.

The maximum thiobencarb residue level in soil from the drainage access to the bayou was 0.14 ppm, and no thiobencarb was recovered from bayou bottom soil.

A maximum thiobencarb residue level of 0.8 ppm was found in aquatic organisms taken by seine collection 2 weeks after application, and then dropped to 0.6 ppm 2 weeks later and the respective residue levels of 4-chlorobenzyl methyl sulfone (a metabolite of thiobencarb) were 0.3 and 0.5 ppm. The thiobencarb residue levels found in caged species were higher then those found in the seine collection. Residues of thiobencarb and 4-chlorobenzyl methyl sulfone reached maximum levels two weeks after application. For example, the thiobencarb residue levels found in Bullhead minnow, striped mullet, and catfish were 3.4, 3.2, and 5.6 ppm, respectively, which dropped to 0.8, 0.1 and 3 ppm, respectively, 19 days after application. The thiobencarb residue levels in organisms taken by trawl collection were generally lower then that found in seine collection and caged species. The thiobencarb residues reached maximum levels 18 days after application (0.35 ppm), whereas the residue levels of 4-chlorobenzyl methyl sulfone were about 0.04 ppm throughout the study period. Therefore, non-target aquatic organisms show a propensity to accumulate thiobencarb residues above the levels found in the water.

In submerged and emerged vegetation, the thiobencarb residue levels ranged from non-detectable to 0.5 ppm, the levels of 4-chlorobenzoic acid ranged from nondetectable to 0.02 ppm, and the level of 4-chlorobenzyl methyl sulfone was nondetectable. The thiobencarb residue level in downwind vegetation within 50 meters of the edge of the treated field ranged from 0.08 to 7.1 ppm, and less than 0.9 ppm was found in vegetation 100 meters or more from the field. No 4-chlorobenzyl methyl sulfone (CBMS) residues were detected in vegetation collected 12 meters or more from the field, and less than 0.08 ppm CBMS was found in vegetation within 12 meters from the field; whereas, the residue levels of 4-chlorobenzoic acid ranged from 0.01 to 0.2 ppm, and 0.1 to 0.9 ppm, respectively. Of all non-vegetation species exposed to Bolero, only canarygrass plant showed visible injury.

3.3 Interim Report Summary of Field Test at Arkansas Rice Experiment Station with Bolero 8 EC, Smith, R., Arkansas Rice Branch Experiment Station, Stuttgart, Arkansas, Sept. 20, 1979, File # 740.01/BOLERO, Acc # 241476, Tab 2.5.

## Procedure

Bolero 8 EC was applied over 40 acres of a preemergent rice crop at a rate of 4 lb ai/A at the Arkansas Rice Branch Experiment Station. Stuttgart, Arkansas. The application was made by air (wind conditions unspecified) to a moist soil on May 8, 1979, five days after planting. The field drains northward into a bar ditch, then from the northwest corner, into a field road ditch that flows ¼ mile down a road into Little La Grue Bayou, and joins Big La Grue Bayou after another 10 miles (Figure 1).

Water was sampled either from within the field or from drainage points, viz., the bar ditch, bottom levee or field outlet, (conflicting accounts as to the exact location of sampling,) at 5, 6, 13, 14, 16, 21, 22, 23, and 34 days after the herbicide application. Immature weeds were sampled 104 days after application; soil samples were taken after the crop was harvested, 132 days after Bolero had been applied. (Any description of sampling procedures or devices used for sampling water, plants or soil is lacking.)

Water samples were stored at ambient temperatures in glass jars with aluminum foil lined lids for variable periods of time before laboratory analysis (up to 14 days storage time). Plant and soil samples were frozen in glass jars until analyzed.

## Methodology

All samples were analyzed by gas chromatography (see all three methodology sections - soil, plant, and water).

## Results

Concentrations of thiobencarb reported in water samples are given in Table 1. The first sampling followed 1.5" of rain five days after application and showed, (as did the 6th day), a mean concentration of 0.33 ppm thiobencarb. After two weeks, (13 and 14 days) the level of thiobencarb had dropped by two-thirds to 0.10 ppm; and it decreased another two-thirds after three weeks to 0.03 ppm (21 and 22 days). Permanent flooding was completed and 7" of rain had fallen before the final water sample was taken (34 days). The residual level was 0.007 ppm at this time.

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Plant samples showed no detectable levels of thiobencarb or its derivative, 4-chlorobenzl methyl sulfone. The soil sampled had a mean residual level of 0.22 ppm thiobencarb, but no 4-chlorobenzl methyl sulfone was detected (Table 2).

Figure 1

Water Drainage of Ricefield Treated at Stuttgart, Arkansas
(Arkansas Rice Branch Experiment Station)

(See BOLERO 8 EC Residue Test Report T-4801)

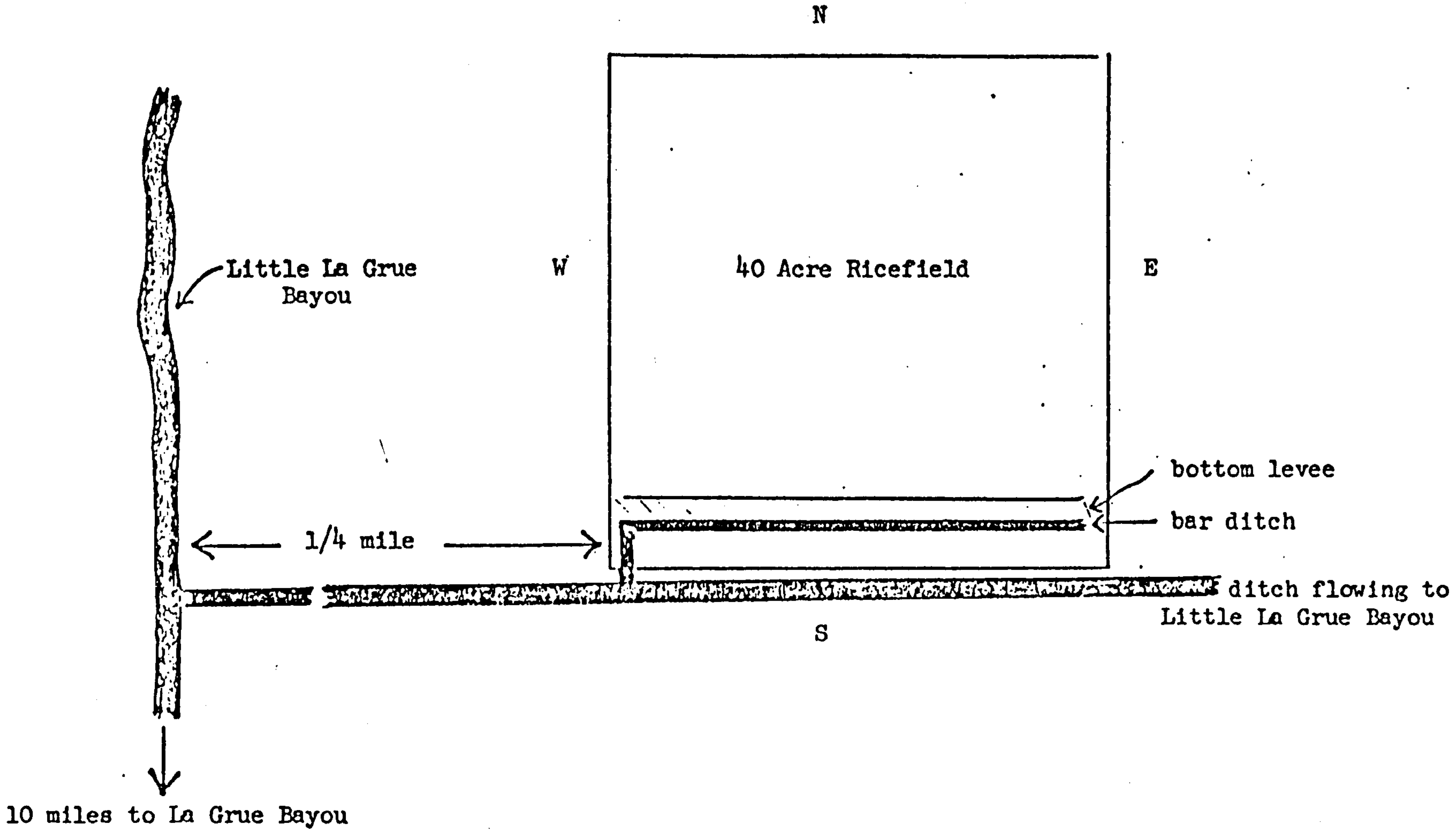

Table 1. Residues (ppm) of thiobencarb in water collected at various locations at various intervals after treatment at 4 lbs active/acre with BOLERO 8EC of a rice field at Stuttgart, Arkansas.

| Sample collection site[a] | ppm Found at various intervals after treatment | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 5 Days | 6 Days | 13 Days | 14 Days | 16 Days | 21 Days | 22 Days | 23 Days | 34 Days |
| Within the field | 0.31 | 0.33 | | | | | | | |
| At field outlet | | | 0.10<br>0.12 | 0.10<br>0.09<br>0.11<br>0.10 | | 0.03<br>0.03 | 0.04<br>0.03 | | 0.006<br>0.007 |
| Bar ditch | | | | | 0.09<br>0.08 | | | 0.04<br>0.04 | |

[a] Location of some of these samples disagrees with field report.

Table 2. Residual herbicide levels in plant and soil samples from Arkansas study.

| Sample | Days after application | Residue (ppm)<br>Thiobencarb | Residue (ppm)<br>4-chlorobenzl methyl sulfone |
|---|---|---|---|
| Immature weeds | 104 | 0 | 0 |
| Soil in rice field | 132 | 0.14 | 0 |
| Soil in rice field | 132 | 0.29 | 0 |

## Conclusions

The chemical fate of this pesticide cannot be adequately evaluated from the information given in this study. Plants, soil and water were sampled in a manner reflecting no experimental design and thus very little useful information was gathered. No description of sampling methods used were provided - lacking even adequate support of control sampling. No initial samples were taken after the application to confirm the amount applied. The report provides no way to estimate the volume of water flowing from the field at the field outlet and therefore, no way to assess the proportion of the applied pesticide that was lost in water draining from the field.

Some conclusions can be surmised. It appears that thiobencarb does not accumulate in immature weeds. A rough estimate of 10% of the thiobencarb applied was recovered in the soil of the treated rice field after harvest, showing that it is fairly recalcitrant in the soil under wet culture rice. If degradation was occurring, the products were either lost through the drainage water (not monitored) or volatilized. Residues of the parent compound leaving the field in the drainage water decline rapidly with time, decreasing in this study by approximately two-thirds each week for the first three weeks.

3.2) Determination of Thiobencarb in Water (RM-I6A-3W), Lai, J.C., Chevron Chemical Company, Ortho Divison, Research and Development Department, February 26, 1979, File # 740.01 BOLERO, Acc. #241479, Tab 4.2.

## Procedure

Thiobencarb in water is extracted with hexane, and the aqueous phase discarded. The hexane phase is filtered through anhydrous sodium sulfate and evaporated to dryness. The residue is dissolved in hexane, and an aliquot is injected into a gas chromatograph with a flame photometric detector.

Recovery data and limit of detection were not provided in this report.

3.5 Determination of Thiobencarb in Soil (RM-16A-35), Elliott, E.J., Chevron Chemical Company, Ortho Division, Research and Development Department, April 2, 1979, File # 740.01/BOLERO, Acc. #241479, Tab. 4.3.

Procedure

Soil is extracted with ethyl acetate, filtered through anhydrous $Na_2SO_4$, then evaporated to dryness. (If clean-up is necessary, the residue is taken up in hexane and collected on an aluminum oxide column. The column is washed with 5% ether in hexane; the thiobencarb is eluted with 15% ether in hexane. The eluate is evaporated to dryness.) Residue is dissolved in ethyl acetate. An aliquot is injected into a gas chromatograph equipped with a flame photometric detector. The limit of detectability is 0.03 ppm.

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3.6 Determination of Thiobencarb and 4-Chlorobenzyl methyl sulfone in Aquatic Organisms Residue Method (RM-16A-3F), Slagowski, J.L., and J.B. Leary, Chevron Chemical Company, Ortho Division, Agricultural Chemical Division, Research and Development Department, August 28, 1979, File #740.01/BOLERO, Acc. #241479, Tab 4.4.

## Procedure

A macerated organism sample was mixed with 5 M phosphoric acid and extracted with ethyl acetate. The ethyl acetate extract was evaporated to dryness after filtering through anhydrous sodium sulfate. The residue was partitioned between hexane and acetonitrile (4:1) and the acetonitrile extract was dried. The residue was then dissolved in cyclohexane containing 15% methylene chloride. The solution was introduced onto an automatic gel Permeation Chromatograph and subsequently on an alumina column for cleanup. The eluate was evaporated to dryness and the residue was then dissolved in benzene. An aliquot was injected into a gas chromatograph equipped with a flame photometric detector. For a 50 g sample, the limits of detectability for thiobencarb and 4-chlorobenzyl methyl sulfone were 0.03 and 0.04 ppm, respectively.

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3.7 Degradation of Benthiocarb in Soils as Affected by Soil Conditions
Nakamura, Y., Ishikawa, K. and Kuwatsuka, S., Laboratory of Soil Science, Nagoya University, Chikusa-ku, Nagoya 464, Japan, J. Pesticide Sci. 2, 7-16, 1977, Acc.# 241479, Tab 5.

Procedure/Methodology

Three soils (Table 1) were each preincubated in the dark under three types of moisture regimes: upland, soil moisture at 40% of the water holding capacity; oxidative flooded, shallow soil layer flooded with 0.5 cm water; reductive flooded, 8 cm of soil covered with 3 cm of water and tightly stoppered. After pre-incubation, $^{14}$C-benthiocarb labeled at the benzene ring dissolved in acetone was added and incubation was continued for 10, 20, 40 and 80 days. Redox potentials were monitored (by an unspecified method).

To determine $^{14}CO_2$ liberated by upland and oxidative flooded conditions, a small vessel of NaOH was included in the flask with the soil. Periodically, $CO_2$ free air was passed through the flask containing the soil and NaOH, on through a trap containing toluene to catch the volatile organics, and through an alkaline scintillation counting solution (Figure 1). Each of these solutions was separately radioassayed for $^{14}$C-activity. After incubation, the soils were acidified with 10 N $H_2SO_4$ and the additional $^{14}CO_2$ liberated was determined. For the reductively flooded samples, a small vessel of NaOH was placed on the soil and aliquots were periodically removed and radioassayed. The soil was transferred to an oxidative apparatus at the conclusion of the incubation period and $^{14}CO_2$ remaining in the soil was determined as above.

Following the $^{14}CO_2$ determinations, the soils were extracted with acetone, the extract neutralized with aqueous NaOH, the acetone evaporated off, and the aqueous solution remaining was extracted with n-hexane. A small portion of the n-hexane solution was radioassayed, the rest was dried with anhydrous $Na_2SO_4$ and analyzed by thin layer chromatography. Following this acetone extraction procedure, the soil residue was extracted with methanol for radioassay. Any radioactivity still remaining in the soil was determined by combustion.

In addition to the major study described, three smaller experiements were performed, using only the kaolin sandy clay loam.

1. Soil was pre-incubated for 2 weeks under upland and oxidative flooded conditions as described previously, then sterilized by autoclaving. Thiobencarb was added and the soils were incubated for designated time periods. A non-sterile control soil was incubated by the same procedure. After incubation, radioactive substances were extracted with methanol instead of acetone. First, a methanol-water extraction (neutral fraction) then methanol-water-$H_2SO_4$ (acid fraction) were collected and radioassayed.

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2. Effects of repeated application were tested. Non-radioactive thiobencarb was added to pre-treated (oxidatively flooded soil). After 2 weeks incubation, $^{14}C$-thiobencarb was added and the incubation continued. The control soil was incubated untreated for the first 2 weeks, then treated with labeled thiobencarb. Successive extracts with methanol, as described for the sterilized soil, were assayed.

3. Pre-incubated soil (oxidatively flooded) was treated with benthiocarb alone or in combination with one other herbicide: simetroyne, CNP, or propanil. The methanol extraction procedure was the same as that described for the sterilized soil experiment.

## Results

About 50% of the applied radioactivity was liberated as $^{14}CO_2$ within 80 days incubation under upland conditions. For oxidative flooded conditions, about one-third of the label was released as $^{14}CO_2$ during the 80 days. The radioactivity of the reductively flooded soils was recovered in the acetone extraction for the most part (∿ 82%) with only small amounts of $^{14}CO_2$ produced (<2%) (Figure 2). The half-life of benthiocarb estimated according to treatments is 20 days under upland conditions; 50 days under oxidative flooded conditions; 200 days under reductive flooded conditions (Figure 3). Changing the incubation from reductive flooded to oxidative flooded conditions resulted in an increased degradation rate that nearly equalled the degradation rate of the continuous oxidative flooded conditions 20 days after the change occurred.

The amounts of radioactive material recovered in the toluene and alkali scintillator (placed as final trap) were reportedly negligible for all soils under all conditions. Levels of radioactivity in the methanol extract and combusted soil residue ranged from 1% to 18% after 80 days (not clearly reported) (Figure 2), and were lowest under reductive flooded conditions (∿2%). Total recovery of radioactivity exceeded 90% for each soil.

Results concerning degradation products are shown in Table 2. For descriptive purposes, only those compounds found at levels greater than 1% will be discussed. Benthiocarb sulfoxide was present under upland and oxidative flooded conditions (1.3% and 2.2%, respectively) on kaolin sandy clay loam soil. Desethylbenthiocarb reached a level of 1.5% on the same soil under reductive flooded conditions. The montmorillonitic clay loam had 4-chlorobenzyl methyl sulfone present at 4% after 40 days, desethylbenthiocarb (1.2%) and benthiocarb sulfoxide (1.1%) under upland conditions; desethylbenthiocarb was 2% under oxidative flooded conditions and no products had levels >1% under reductive flooded conditions. The humic silty clay soil had repeatedly high levels of desethylbenthiocarb (1.1 and 2.5%), 4-chlorobenzylmethyl sulfone (1.8 and 1.7%) and benthiocarb sulfoxide (2.8%) under upland conditions. Under oxidative flooded conditions, desethylbenthiocarb reached a level of 1.5%, and none of the degradation products were >1% under reductive flooded conditions for this soil.

Sterilized soil degraded approximately 3% of the applied radioactivity, liberating approximately that amount as $^{14}CO_2$ after 40 days under both upland and oxidative flooded conditions. Non-sterile controls liberated 43-63% of the applied radioactivity as $^{14}CO_2$ under those conditions.

The addition of 20 ppm benthiocarb in two applications, two weeks apart, showed a degradation rate of 4 ppm $^{14}C$-benthiocarb in 20 days, no different from the single 10 ppm application (Figure 4). No effect on the degradation rate of benthiocarb was observed when other herbicides were present (Figure 5).

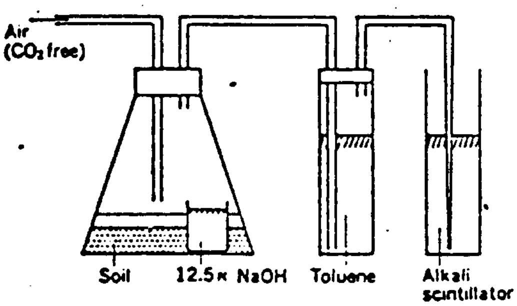

Figure 1. Apparatus for the determination of liberated $^{14}CO_2$.

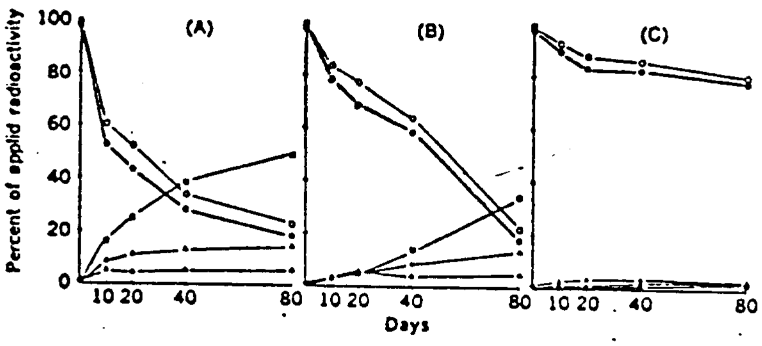

Figure 2. Changes in the radioactivity levels under upland (A), oxidative flooded (B), and reductive flooded (C) conditions in kaolin silty clay loam soil.

o acetone extracts, Δ MeOH extracts, ▲ soil residue
■ $^{14}CO_2$, ● benthiocarb

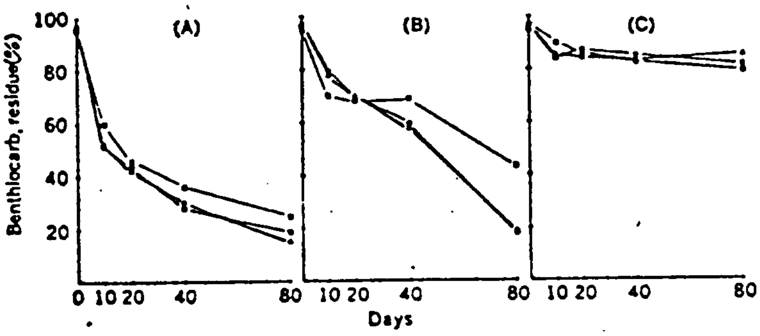

Figure 3. Degradation of benthiocarb in three different soils under upland (A), oxidative flooded (B), and reductive flooded (C) conditions.

● Anjo soil, ▲ Nagano soil, ■ Tochigi soil

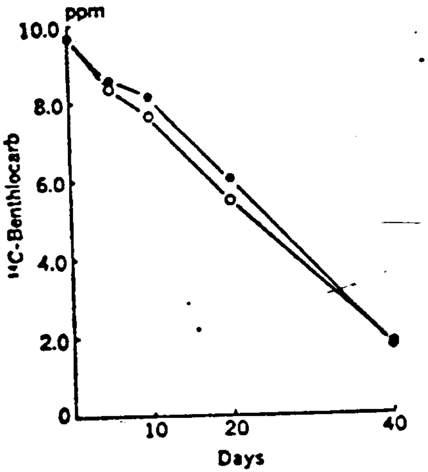

Figure 4. Degradation of $^{14}C$-benthiocarb applied 2 weeks after pretreatment with or without nonradioactive benthiocarb in soil.

● pretreatment with nonradioactive benthiocarb, ● without nonradioactive benthiocarb

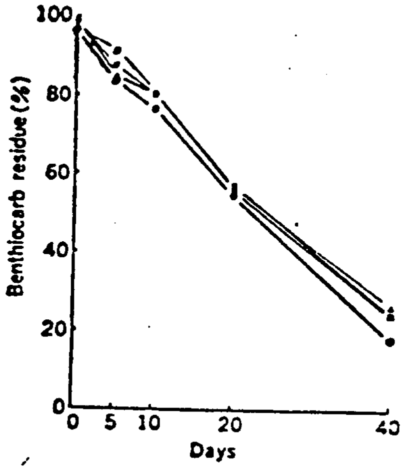

Figure 5. Degradation of benthiocarb in soil with simetryne, CNP, and propanil.

● benthiocarb only, ▲ with simetryne,
■ with CNP, ▼ with propanil

Table 1. Properties of soils used.

| | Sandy Clay Loam | Clay Loam | Silty Clay |
|---|---|---|---|
| Clay mineral | kaolin | montmorillonite | allophane |
| Clay content (%) | 23.1 | 20.5 | 5.4[a] |
| pH | 6.1 | 5.2 | 5.6 |
| CEC (meq/100g) | 13.6 | 21.3 | 40.5 |
| Total carbon (%) | 1.93 | 1.81 | 7.87 |

[a] Probably typographical error in report.

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Table 2. Timecourses of degradation products in the n-hexane extracts from three soils (percent of applied radioactivity).

| | | Conditions | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Upland | | | | Oxidative flooded | | | | Reductive flooded | | | |
| Degradation products | days | 10 | 20 | 40 | 80 | 10 | 20 | 40 | 80 | 10 | 20 | 40 | 80 |
| Kaolin SCL | | | | | | | | | | | | | |
| 2-Hydroxybenthiocarb | | 0.3 | 0.2 | 0.2 | tr. | 0.2 | 0.4 | 0.2 | tr. | 0.3 | 0.4 | 0.6 | 0.2 |
| Desethylbenthiocarb | | 0.6 | 0.5 | 0.4 | 0.2 | 0.7 | 0.8 | 0.7 | 0.2 | 1.5 | 0.8 | 0.5 | tr. |
| 4-Chlorobenzoic acid | | 0.8 | 0.3 | 0.2 | 0.2 | 0.2 | 0.5 | 0.2 | 0.1 | 0.2 | 0.2 | 0.3 | 0.2 |
| 4-Chlorobenzyl methyl sulfone | | 0.4 | 0.6 | 0.3 | 0.2 | tr. | 1.1 | tr. | tr. | tr. | tr. | tr. | tr. |
| Benthiocarb sulfoxide | | 0.2 | 1.3 | 0.9 | tr. | tr. | 2.2 | 1.1 | 1.0 | tr. | tr. | 0.3 | 0.2 |
| Other spots | | 2.0 | 0.9 | 0.7 | 0.6 | 2.4 | 2.0 | 1.1 | 0.5 | 1.5 | 1.3 | 0.7 | 0.1 |
| Montmorillinitic CL | | | | | | | | | | | | | |
| 2-Hydroxybenthiocarb | | 0.4 | 0.7 | 0.3 | 0.1 | 0.3 | 0.6 | 0.5 | 0.2 | 0.3 | 0.3 | 0.3 | 0.2 |
| Desethylbenthiocarb | | 0.5 | 1.2 | 0.4 | 0.1 | 0.7 | 2.0 | 0.6 | 0.3 | 0.1 | 0.1 | 0.2 | 0.3 |
| 4-Chlorobenzoic acid | | 1.0 | 0.4 | 0.4 | 0.2 | 0.2 | 0.4 | 0.4 | tr. | 0.2 | 0.1 | 0.3 | 0.1 |
| 4-Chlorobenzyl methyl sulfone | | 0.7 | 0.2 | 4.0 | 0.1 | tr. | tr. | tr. | tr. | tr. | tr. | tr. | 0.1 |
| Benthiocarb sulfoxide | | 0.2 | 0.1 | 1.1 | 0.9 | tr. | tr. | tr. | tr. | tr. | tr. | tr. | 0.2 |
| Other spots | | 1.8 | 3.4 | 0.7 | 0.1 | 1.8 | 2.0 | 1.5 | 0.3 | 0.4 | 0.4 | 0.5 | 0.2 |
| Humic SiC | | | | | | | | | | | | | |
| 2-Hydroxybenthiocarb | | 0.3 | 1.0 | 0.4 | tr. | 0.4 | 0.5 | 0.7 | 0.5 | 0.3 | 0.2 | 0.2 | 0.2 |
| Desethylbenthiocarb | | 1.1 | 2.5 | 1.0 | 0.4 | 0.2 | 1.5 | 0.9 | 0.1 | 0.2 | 0.2 | 0.3 | 0.2 |
| 4-Chlorobenzoic acid | | 0.3 | 0.4 | 0.5 | tr. | tr. | 0.2 | 0.5 | 0.3 | tr. | tr. | tr. | 0.2 |
| 4-Chlorobenzyl methyl sulfone | | tr. | tr. | 1.8 | 1.7 | tr. | tr. | tr. | 0.8 | tr. | tr. | tr. | tr. |
| Benthiocarb sulfoxide | | tr. | tr. | tr. | 2.8 | tr. | tr. | tr. | 0.2 | 0.3 | 0.4 | 0.2 | 0.2 |
| Other spots | | 1.7 | 3.0 | 2.2 | 0.3 | 1.7 | 2.6 | 2.1 | 0.8 | 0.1 | 0.1 | tr. | 0.3 |

Tr.: trace amounts (less than 0.1%).

## Conclusions

Redox conditions of the field, (upland, oxidative flooded or reductive flooded,) are a key factor affecting the rate of degradation and the degradation compounds produced from benthiocarb. Physico-chemical soil factors have comparatively little effect (Figure 3). Quantitative statements of these results are not substantiated because it appears that the experiments were run with no replication of the experimental units. Thus, absolute comparisons amongst soils or treatment conditions are not justified. Relatively however, the higher the redox potential, the faster the degradation process.

Results presented concerning various sources of radioactivity recovered show that complete oxidation to $^{14}CO_2$ was occurring under upland conditions, and to a lesser extent under oxidative flooded conditions, but hardly, if at all, under reductive flooded conditions. As only negligible radioactivity was found in the toluene traps, it can be assumed that volatilization of benthiocarb or its degradative products is low. Evidence for a fraction of benthiocarb "fixed" gradually in the soil is shown in Figure 2(a) and (b) for the kaolin mineral soil. After 80 days, around 18% of the radioactivity applied was found in the soil residue of upland and oxidative flooded soils by combustion after the other extractions.

The degradation compounds derived from benthiocarb will vary greatly with time, soil type and redox conditions of the soil. The degradation product found in the largest quantity throughout the 80 days in both oxidative and reductive flooded conditions across all soils was desethylbenthiocarb, except for the kaolin soil under oxidative flooded conditions which was higher in benthiocarb sulfoxide. Under upland conditions, benthiocarb sulfoxide was again dominant in the kaolin soil, while the montmorillonitic soil was highest in 4-chlorobenzyl methyl sulfone and the humic soil was high in the forementioned sulfone, sulfoxide and desethylbenthiocarb. The greatest amount of degradative products, in general, was found under upland conditions, and then, generally after 40 days time. Under reductive flooded conditions, only small quantities of degradation compounds are formed.

Microbial activity, not non-biological chemical reactions, initiates the degradative processes of benthiocarb as the sterile soil clearly shows. Herbicides not affecting benthiocarb degradation include simetryne, CNP and propanil. A second application of benthiocarb soon after the first does not affect the degradation rate.

3.8 Photodegradation of Benthiocarb Herbicide, Ishikawa, K., Y. Nakamura, Y. Nike, and S. Kuwatsuka. Laboratory of Soil Science, Faculty of Agriculture, Nagoya University. 1977. J. Pesticide Sci. 2:17-25. Acc. #241479, Tab 6.

Procedure/Methodology

Three benthiocarb preparations, one $^{14}C$-labeled at the benzene ring, one $^{14}C$-labeled at the benzyl-methylene carbon, and an unlabeled compound were used in these studies.

Degradation of non-labeled benthiocarb was investigated using a low pressure mercury lamp (maximum intensity at 254 nm), immersed in aqueous solutions (15 ppm) of benthiocarb. At various intervals during 80 minutes of irradiation, solution was taken and extracted with ether, the extract dried and concentrated, and an aliquot analyzed by gas chromatography for benthiocarb, 4-chlorobenzyl alcohol, and 4-chlorobenzaldehyde. Similar experiments with several other pesticides (BPMC, EPTC, fenitrothion, IBP, propanil, simstryne and swep) were conducted for comparison of degradation rates. Gas chromatography/mass spectrometry (GC-MS) investigation of benthiocarb degradation under the low-pressure mercury lamp was also conducted, by pooling aqueous solutions of non-labeled benthiocarb (initial concentration 10 ppm) after 20 minutes of irradiation, to provide a total of 10 liters of solution. n-Hexane and ether extracts of the solution were then analyzed by GC-MS for benthiocarb degradation products.

The degradation of benzene ring-labeled benthiocarb was investigated under a high pressure mercury lamp (maximum intensity at 365 nm). Aqueous solutions of the compound (10 ppm) were irradiated from a distance of 17 cm, and aliquots of the solution taken at intervals for up to 120 hours. Aqueous and ether extracts were assayed for radioactivity, and concentrates of the ether extracts chromatographed on TLC plates.

The degradation of benthiocarb under natural sunlight was studied using benzyl-methylene labeled benthiocarb (10 ppm) in covered and uncovered Petri dishes. Dishes were weighed every two hours, at which time aliquots of the solutions were taken and analyzed for radioactivity by liquid scintillation. Degradation products were determined by TLC of concentrated ether extracts.

Degradation of benthiocarb on glass plates during ultraviolet irradiation was studied by spreading 10 mg of benzene-ring labeled benthiocarb dissolved in n-hexane on a glass plate, and evaporating the solvent. Plates were exposed 10 cm below the high pressure mercury lamp for periods ranging from 45 minutes to 47 hours. After irradiation, plates were washed in a mixture of acetone and ether, and immersed in water to dissolve polar products.

Aliquots of these polar and organic solutions were assayed for radioactivity, and aliquots of the organic solution chromatographed on TLC plates for identification of degradation products.

Results

Experiments with aqueous solutions of non-radiolabeled benthiocarb (15ppm) showed a half-life of approximately 10 minutes for the compound following irradiation by the low pressure mercury lamp. 4-Chlorobenzyl alcohol and 4-chlorobenzaldehyde were major photoproducts, increasing to 10 and 20% of the added benthiocarb, respectively, before declining (Figure 1 ). Degradation of aqueous benthiocarb was more rapid than that of the seven other pesticides studied under similar conditions. GC-MS analysis of benthiocarb solutions exposed to the low pressure mercury lamp for 20 minutes revealed at least 40 degradation products, 32 of which were unidentified. Identified compounds were 4-chlorobenzyl alcohol, 4-chlorobenzaldehyde, 4-chlorobenzoic acid, 4-chlorobenzyl diethylamine, 4-chlorobenzyl N,N-diethylcarbamate, methyl N,N-diethylcarbamate, and 4-chlorobenzyl ethylamine.

Degradation of benzene ring-labeled benthiocarb in aqueous solution (10 ppm) under the high pressure mercury lamp occurred at a rate similar to that found with the low pressure mercury lamp. The formation of polar degradation products was indicated by an increase in unextractable radioactivity, which represented more than 20% of the added radioactivity after 120 minutes of irradiation. Total radioactivity declined approximately 15% during 120 minutes of irradiation. Loss was attributed to evaporation of benthiocarb degradation products, especially 4-chlorobenzaldehyde. More than 10 products were detected by TLC, with the following compounds being identified: desethyl benthiocarb, benthiocarb sulfoxide, 4-chlorobenzyl alcohol, 4-chlorobenzaldehyde, 4-chlorobenzoic acid, bis (4-chlorobenzyl) sulfide, 4-chlorobenzyl diethyl amine, 4-hydroxybenzyl-esters of N-ethyl and N,N-diethylthiolcarbamic acids, 4-hydroxybenzyl alcohol, 4-hydroxybenzaldehyde and 4-hyroxybenzoic acid. After 120 minutes only 4-chlorobenzaldehyde exceeded 10% of the originally applied radioactivity, with 4-chlorobenzyl alcohol and 4-chlorobenzoic acid each representing approximately 6% of the applied radioactivity. Benthiocarb sulfoxide increased to approximately 8% of the applied radioactivity during the first 30 minutes of irradiation, but rapidly declined thereafter, suggesting that the compound was an intermediate product. None of the other identified compounds represented more than 1% of the initial radioactivity.

Experiments with benzyl-methylene labeled benthiocarb in solution (10 ppm) under natural sunlight showed that radioactivity and water were rapidly lost from uncovered Petri plates as compared with covered plates (Table 1). Radioactivity remaining in the uncovered plates was primarily the parent compound. The relationship observed between the amount of water lost and the loss of radioactivity suggested that codistillation was occurring. TLC data showed

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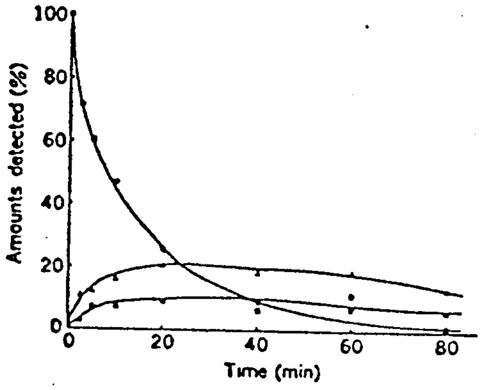
the formation of desethyl benthiocarb, 4-chlorobenzyl alcohol, 4-chlorobenzoic acid, and benthiocarb sulfoxide in both covered and uncovered irradiated solutions, but none of these compounds represented more than 4.5% of the initial radioactivity. At least six unidentified compounds were noted, none representing more than 10% of initial activity.

Irradiation of benthiocarb on glass plates under a high pressure mercury lamp resulted in the formation of six degradation products: 4-chlorobenzaldehyde, 2-hydroxybenthiocarb, desethyl benthiocarb, 4-chlorobenzyl alcohol, 4-chlorobenzoic acid and benthiocarb sulfoxide. With the exception of 4-chlorobenzoic acid, which represented up to 29% of the original activity, none of these compounds accounted for more than 4% of the original activity. Unknowns accounted for up to 22% of the original activity. Approximately 56% of applied radioactivity was lost after 47 hours of irradiation and attributed to the formation of volatile products.

Figure 2 presents a possible photodegradation pathway of benthiocarb proposed by the authors.

Figure 1. Degradation of benthiocarb and formation of 4-chlorobenzyl alcohol and 4-chlorobenzaldehyde by irradiation with ultraviolet rays with maximum intensity at 254 nm.



● benthiocarb

■ 4-chlorobenzyl alcohol

▲ 4-chlorobenzaldehyde

Results were expressed in terms of molar percent.

Figure 2. Possible photodegradation pathway of benthiocarb.

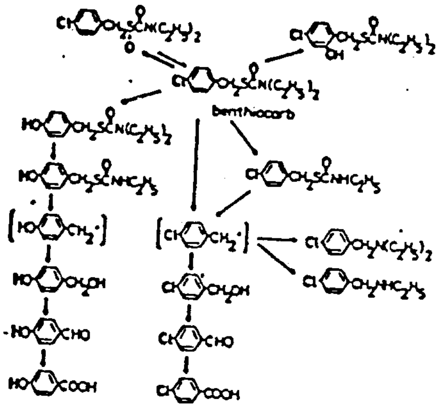


Table 1. Changes in the level of radioactivity and in the volume of water under exposure to sunlight.[a]

| Exposure time (hr) | A | | B | |
|---|---|---|---|---|
| | Radio-activity | Water (ml) | Radio-activity | Water (ml) |
| 0 | 100 | 150 | 100 | 150 |
| 2 | 97.8 | 149 | 87.6 | 133 |
| 4 | 95.0 | 147 | 75.7 | 113 |
| 6 | 90.8 | 144 | 57.0 | 93 |
| 8 | 85.2 | 140 | 42.9 | 73 |
| 10 | 82.4 | 138 | 30.4 | 52 |
| 12 | 79.6 | 135 | 14.9 | 28 |

[a] 150 ml of the benthiocarb aqueous solution was exposed to sunlight with (A) or without (B) a quartz cover glass. Every 2 hours the vessels were weighed and an aliquot of each solution was pipetted for radioassay. The radioactivity levels and amounts of water are expressed in percent of initial amount and in volume (ml), respectively.

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## Conclusions

Benthiocarb in aqueous solution dissipates rapidly via photodegradation and volatilization (codistillation) of the parent compound and/or degradation products, with an observed half-life of approximately 10 minutes under UV light from high and low pressure mercury lamps. Benthiocarb on glass plates dissipates more slowly upon exposure to UV light, where approximately 44% of the applied radioactivity remained after 47 hours. Although approximately 15 degradation products have been identified (and more than 20 unidentified), only 4-chlorobenzyl alcohol (10%), 4-chlorobenzaldehyde (20%), and 4-chlorobenzoic acid (29%) were found in these experiments to represent 10% or more of the original benthiocarb.

The design of most of the experiments reported here is not sufficient to determine the relative importance of photodegradation versus volatilization in the loss of benthiocarb from aqueous solutions. Preliminary data from the experiment conducted in covered and uncovered petri dishes containing aqueous solution of benthiocarb suggest that volatilization is the predominant route of dissipation.

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## 3.9 Volatilization of Benthiocarb Herbicide from the Aqueous Solution and Soil,

Ishikawa, K., Y. Nakamura, and S. Kuwatsuka, Laboratory of Soil Science, Faculty of Agriculture, Nagoya University, 1977, J. Pesticide Sci. 2:127-134. Acc. #241479, Tab 7.

### Procedures/Methodology

Volatilization of benthiocarb from aqueous solution and from flooded and unflooded soils following exposure to sunlight was investigated. Benthiocarb, radiolabeled with $^{14}C$ at either the benzene-ring or the benzyl-methylene carbon was used.

Benthiocarb, labeled at the benzyl-methylene carbon, was used to study volatilization of the compound from aqueous solution. Benthiocarb solutions (10 ppm) were placed in each of two petri dishes, one of which was covered with a glass plate. Dishes were exposed to the sun (data and location not indicated) for two days; during the night both dishes were covered and placed in a dark room at 20 C. Dishes were weighed every two hours to determine the amount of solution, and aliquots were taken for radioactivity counts by liquid scintillation counting.

Experiments to determine the effect of soil on volatilization of aqueous benthiocarb were conducted by mixing 200 ml of water with each 50 g dry soil sample (sandy clay loam: clay content 23%; total carbon 1.9%; CEC 13.6 meq/100 g), and allowing to stand at room temperature for 20 days. Labeled benthiocarb (position of the $^{14}C$-label not described) mixed in acetone with unlabeled benthiocarb, was added to the surface water of the above samples to establish an aqueous concentration of 10 ppm. Samples were placed under sunlight for 6 hours, and radioactivity of the surface water and soil determined every two hours during exposure to sunlight.

Additional laboratory experiments were conducted to investigate the loss of benthiocarb under different soil treatment applications. Labeled benthiocarb (position of the label not indicated) was dissolved in water together with an unlabeled emulsifiable concentrated formula containing 50% benthiocarb as active ingredient. Then, 10.5 ml of this benthiocarb solution (1.1 mg benthiocarb) was added a) to the surface water of flooded soil (100 g soil + 100 g water, mixed and allowed to stand 1 week before treatment); b) to soil surface, by spraying uniformly on 100 g of soil adjusted to 60% of the maximum water holding capacity, or c) by incorporation into the soil (same as b, but the soil mixed after spraying). A reference sample was also run, in which 10.5 ml of the benthiocarb solution was mixed with 100 ml water containing glass beads. The above samples were placed in separate dessicators, and exposed to the sun for up to 7 days. Beakers containing liquid paraffin were placed in each dessicator to trap volatile lipiphillic compounds. Aliquots of the liquid paraffin were taken at various intervals (2, 4, and 5 hours, 1, 2, 3, and 7 days) of exposure and assayed for radioactivity.

Identification of volatile compounds resulting from exposure of benthiocarb aqueous solution to sunlight was also conducted. A falsk containing 10 ppm labeled benthiocarb (position of label not indicated) solution was exposed to sunlight, and volatile products were carried in an air flow through a water-cooled condenser. Condensates were collected in a flask, and uncondensated residual materials were collected in n-propyl alcohol. The benthiocarb solutions were exposed to the sun for 5 days (12 h/day), at 40,000-12,000 lux. The relative importance of photodegradation versus volatilization in the formulation of products was determined by conducting similar experiments in the absence of air flow, but in the presence of light; and in the presence of air flow, but in the absence of light (a brown glass flask containing the benthiocarb solution was used instead of colorless pyrex, eliminating ultraviolet and most visible light). The identification of trapped volatile products was conducted by thin-layer chromatography.

## Results

The effect of sunlight on aqueous solutions of benthiocarb in covered and uncovered petri dishes is presented in Figure 1. Water loss in the covered dish after 12 hours was less than 10% but exceeded 80% in the uncovered dish. The decrease in radioactivity was approximately proportional to the decrease in water.

Experiments conducted to determine the effect of soil on volatilization of benthiocarb from aqueous solution showed that soil retarded the volatilization of radioactive compounds when compared with the control system (glass beads). Radioactivity in the surface water decreased approximately 70% after 6 hours of exposure, with a large portion of the initial activity (approximately 63%) being absorbed by the soil.

Data showed that benthiocarb was more readily lost from flooded soil than from unflooded soil (Table 1) and was not readily lost from the reference solution (containing glass beads). Less than 2% of the applied radioactivity was recovered in the liquid paraffin traps from the upland (unflooded) soils after 7 days of exposure, but 6.5 and 10.4% of the original activity was recovered from the flooded and reference solution, respectively. The comparatively small amount of benthiocarb volatilized from unflooded soils was attributed to adsorption of benthiocarb on soil particles.

Experiments conducted to identify products volatilized from aqueous benthiocarb solution upon exposure to sunlight showed that approximately 60% of the volatilized radioactivity was parent compound. The remainder consisted of volatile photoproducts of which 4-chlorobenzaldehyde was predominant (but not quantifiable due to a large loss of the aldehyde, due to its high volatility, during concentration of the extract). Photoproducts other than the aldehyde were not identified. The amounts of radioactivity lost from the colorless and brown flasks were comparable (7.3 and 5.7% of original, respectively). No radioactivity was detected in any of the volatile traps in the absence of air flow.

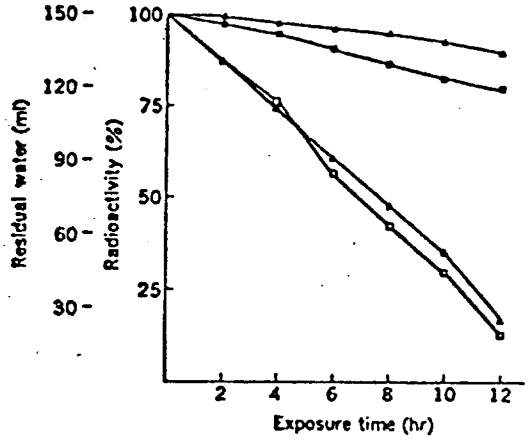

Figure 1. Residual amounts of benthiocarb solution and radioactivity under exposure to sunlight.

▲ Residual water with a quartz glass plate,
△ Residual water without a quartz glass plate,
■ Radioactivity with a quartz glass plate,
□ Radioactivity without a quartz glass plate.

Table 1. Volatility of benthiocarb under various soil conditions.*

| Method of adding $^{14}$C-benthiocarb | Trapped radioactivity(%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | hrs | | | days | | | |
| Exposure time → | 2 | 4 | 6 | 1 | 2 | 3 | 7 |
| Reference solution | 0.2 | 0.5 | 0.8 | 1.5 | 4.0 | 5.5 | 10.4 |
| Added to surface water of flooded soil | 0.3 | 0.8 | 0.9 | 1.9 | 2.8 | 4.1 | 6.5 |
| Sprayed on upland soil | 0.2 | 0.3 | 0.3 | 0.7 | 0.8 | 1.2 | 1.7 |
| Incorporated into upland soil | 0.1> | 0.1> | 0.1 | 0.2 | 0.1 | 0.2 | 0.2 |

* Values are expressed in terms of percent of the applied radioactivity.

## Conclusions

Benthiocarb in aqueous solution is rapidly lost on exposure to sunlight, the loss being proportional to the amount of water evaporated. This loss is primarily through direct volatilization of the parent compound, although the formation of more highly volatile photoproducts such as 4-chlorobenzaldehyde also occurs.

Benthiocarb volatilization from aqueous solution is retarded in the presence of soil, probably due to the adsorption of the herbicide on soil particles. Volatilization of the compound from unflooded soils is reduced compared with volatilization from flooded soils, and soil incorporation of the chemical greatly reduces volatilization. These data indicate that loss of benthiocarb from water will be maximized by the present practice of applying the chemical directly to surface waters of paddy fields.

4.

# ENVIRONMENTAL FATE ANALYSIS

In aqueous solution, thiobencarb dissipates rapidly via volatilization (codistillation) and photodegradation. (No hydrolysis studies were reviewed in this packet.) The major route of dissipation appears to be the volatilization of the parent compound (at a rate proportional to the rate of volatilization of the water), although the formation of more highly volatile compounds via photodegradation, such as 4-chlorobenzaldehyde, also contribute to the dissipation. Under UV light, the observed half-life of thiobencarb in aqueous solution is approximately 10 minutes. Volatilization is retarded in the presence of soil; thus volatilization is fastest under flooded soil conditions and slowest when thiobencarb is incorporated into unflooded soil.

Soil metabolism of thiobencarb by microorganisms is affected more by the redox potential of the soil than by other soil physico-chemical properties. Microbial degradation is fastest in well aerated "upland" soils, where oxidation of the thiobencarb ring to $CO_2$ occurs with a half-life of approximately 80 days. In soils that are reductively flooded (maintained in an anaerobic state), <2% of the ring-labeled activity would be expected to be released as $^{14}CO_2$ in 80 days. The major metabolites, desethylbenthiocarb, benthiocarb sulfoxide, and 4-chlorobenzyl methyl sulfone, will be present at times during the metabolism, reaching a few percent of the applied amount in upland soils and generally a few tenths of a percent in reductively flooded soils.

At normal field application rates, thiobencarb residues dissipate fairly rapidly from the soil and water of flooded rice fields. Soil concentrations (surface 1.5 inches) decline about 90% during the first 2 weeks after an application. There are some indications that low levels of thiobencarb (0.22 ppm) remain "fixed" in the soil for long periods of time (present 132 days after application) under typical alternating flood and drain conditions. With frequent flooding and draining of a rice field, residues of the parent compound leaving the field in drainage water decline by approximately 90% in 2 weeks.

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Nontarget aquatic organisms have a propensity for accumulating thiobencarb, ranging from 10 to 80 times greater than the ambient water concentration. The bioconcentrations are highest 2-3 weeks after the pesticide's application, with a mean residue level of 0.8 ppm (averaged from over 21 aquatic species collected by seine). Caged fish tend to accumulate higher residues, notably the caged catfish and striped mullet, with mean concentrations of 5.6 and 3.2 ppm, respectively (ambient water averaged 0.04 ppm). Residues of the metabolite 4-chlorobenzyl methyl sulfone can be expected to range between 0.04 and 0.5 ppm.

Of all the nontarget levee vegetation affected by an aerial application of thiobencarb (at 4 lb ai/A in this one study), only canary grass is expected to show visible symptoms of injury (around 50% reduction in growth). Residue levels in submerged and emerged vegetation will vary between nondetectable (<0.01 ppm) and 0.5 ppm thiobencarb when the average concentration in the water is 0.04 ppm. Very low levels (<0.02 ppm) of 4-chlorobenzoic acid may be found and no 4-chlorobenzyl methyl sulfone is expected to be present. Downwind vegetation may contain residues ranging from 0.08 to 7.0 ppm thiobencarb, with levels generally decreasing with increasing distance from the site of application.

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## 5. RECOMMENDATIONS

5.1 We concur with the registration of the Bolero 8EC.

5.2 We do not concur with the registration of the Bolero 10G since it lacks a 6 month rotational crop restriction.

5.3 Adverse effects, 6(a)(2), were not found in the data.

Samuel M. Creeger June 10, 1980

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Review Section #1
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