

US EPA ARCHIVE DOCUMENT

EEEE BRANCH REVIEW

DATE: IN \_\_\_\_\_ OUT \_\_\_\_\_ 3/14/78  
IN 5/23/78 OUT 5/26/78 IN \_\_\_\_\_ OUT \_\_\_\_\_  
FISH & WILDLIFE ENVIRONMENTAL CHEMISTRY EFFICACY

FILE OR REG. NO. 100-100

PERMISSION OR EXP. PERMIT NO. \_\_\_\_\_

DATE DIV. RECEIVED 3/3/78

DATE OF SUBMISSION \_\_\_\_\_ 3CID-2A-Yes

DATE SUBMISSION ACCEPTED \_\_\_\_\_

TYPE PRODUCT(S): (I) D, H, F, N, R, S \_\_\_\_\_

PRODUCT MGR. NO. 16 - Gee

PRODUCT NAME(S) Curacron 6E

COMPANY NAME Ciba-Geigy Corporation

SUBMISSION PURPOSE Registration on cotton

CHEMICAL & FORMULATION O-(4-bromo-2-chlorophenyl) O-ethyl  
S-propyl phosphorothioate

1.0 Introduction

1.1 Active ingredient: 0-(4-Bromo-2-chlorophenyl)-0-ethyl-5-propyl phosphorothioate 59.6%. Curacron 6E contains 6 lbs. a.i./gallon.

1.2 Curacron, CGA-15234

1.3 Applicant proposes registration of Curacron 6E for insect control on cotton. Also revised or additional data sent 5/23/78 Acc #233984.

1.4 Other reviews:

100-EUP-53	2/1/77 and 7/19/77
100-EUP-53 and 56	7/19/77

2.0 Directions for Use

2.1 Cotton bollworm, tobacco budworm, cotton leafperforator, beet armyworm - Apply on a 5 - 7 day schedule starting when larvae first appear. Use 2/3 - 1 pt. per acre on light to moderate infestations and 1 - 1 1/3 pts. per acre on moderate to heavy infestations.

2.2 Cotton boll weevil - Apply 2/3 - 1 1/3 pts of Curacron 6E plus either 1/2 - 1 pt of Guthion®2L or 1/2 - 1 pt. of methyl parathion 4E per acre. Use the low rate of either Guthion or methyl parathion for light to moderate infestations and the high rate for moderate to heavy infestations.

2.3 Apply in a minimum of 5 gals of spray per acre with ground equipment or in a minimum of 1 gal. of spray per acre by air.

2.4 This product is highly toxic to bees exposed to direct treatment or residues on crops. Protective information may be obtained from your Cooperative Agricultural Extension Service.

2.5 Note: Do not apply more than 4 qts. of Curacron 6E per acre per season nor apply within 14 days before harvest. Do not apply Guthion or methyl parathion alone within 14 days of harvest after applying Curacron tank mixed with these materials. Do not graze treated cotton plants or feed gin waste.

2.6 Refer to Guthion 2L and methyl parathion 4E labels for further directions, limitations, and precautions.

2.7 Fields treated with Curacron may be rotated to other crops.

2.8 Environmental Hazards

This pesticide is toxic to fish and wildlife. Use with care when applying to areas frequented by wildlife or adjacent to any body of water. Keep out of lakes, streams, or ponds. Do not apply when weather conditions favor drift from treated areas. Apply this pesticide only as specified on this label. Do not contaminate water by cleaning of equipment or disposal of wastes.

2.9 Storage and Disposal

Do not store near food or feed. Do not contaminate water, food, or feed by storage or disposal. Open dumping is prohibited. Do not reuse empty container. Pesticide, spray mixture, or rinse water that cannot be used or chemically reprocessed should be disposed of in a landfill approved for pesticides or buried in a safe place away from water supplies. Triple rinse and discard in an approved landfill or bury in a safe place.

3.0 Discussion of Data

3.1 Hydrolysis Data

3.1.1 Hydrolysis of CGA-15324. K. Huhtanen, p. 22, Feb. 20, 1978. Cannon Labs, Inc. Vol. 2 of 9, Acc. #096857, 8F2057.

In response to recommendations from a previous hydrolysis review (see #100-EUP-53, Feb. 1, 1977) the applicant is reporting data on hydrolysis conducted at 1.0 ppm at pH 5, 7 and 7 and temperatures of 5, 30 and 70°C.

Conclusions

1) This study alone is not acceptable without a protocol or methodology section. All that was sub-

mitted with this experiment was a letter from Cannon Labs to Ciba-Geigy and one table of data with 2 graphs. Degradation products were not identified and a material balance was not submitted.

- 2) We do conclude hydrolysis of CGA-15324 is rapid and increases with higher temperatures and pH values.
- 3) The reported hydrolysis rates are similar to those found with 10 ppm CGA-15324.

### 3.2 Aerobic Soil Metabolism

#### 3.2.1 The metabolism of $\phi$ - $^{14}\text{C}$ -CGA-15324 Streaked on Lettuce Leaves and the Degradation of This Compound in Soil, GAAC-74078, 8F2057 vol 3 of 6, acc #096852.

Two week old Salad Bowl leaf lettuce was transplanted to buckets, 2 plants per bucket, containing silt loam soil (28.8% sand, 66.4% silt, 14.8% clay, 3.6% OM, pH=5.7, CEC=8.4). At 5 weeks of age, the upper lettuce leaves were streaked with an ethanolic solution of  $^{14}\text{C}$  ring labeled curacron at 2 mg/plant and the soil was treated at 4 mg/0.546 ft<sup>2</sup> (0.7 lb ai/A).

Lettuce and soil were sampled during the next 2 weeks. Plant samples were extracted to give organic, polar and non-extractable fractions (AG-214 and AG-156) followed by 2-dimensional TLC (AG270). Soil was extracted with methanol and water followed by ionic characterization of the extractables (AG-156).

#### Results

##### 1) Metabolism of $\phi$ - $^{14}\text{C}$ -CGA-15324 by Leaf Streaked Lettuce

Interval (Days)	0	7	14	21
<u>Total ppm</u>	310.27	325.58	168.29	171.27
<u>Balance</u>	<u>Radioactive Distribution in Percent</u>			
Organic	95.2	67.6	69.8	72.9
Polar	3.0	21.7	23.5	11.0
Non-extractable	<u>1.8</u>	<u>10.8</u>	<u>6.7</u>	<u>16.1</u>
Total	100.0	100.1	100.0	100.0

#### Ionic Characterization of Polar Fraction

Acids	2.9	21.3	23.4	9.2
Bases	0	0.1	0.1	0.5

Neutrals	0	0.2	0.1	1.3
Zwitterions	<u>0.1</u>	<u>0.1</u>	<u>0</u>	<u>0</u>
Total	3.0	21.7	23.6	11.0

2) Quantitation of the Metabolites of  $\phi$ - $^{14}\text{C}$ -CGA-15324 in the Extractables

Interval (Days)	0	7	14	21
Extractable Radioactivity (ppm)	304.59	290.50	157.06	143.73
<u>Characterization</u>	<u>Radioactive Distribution in Percent</u>			
CGA-15324	91.8	64.8	68.1	61.1
4-bromo-2-chloro-phenol	0.9	2.2	0.8	10.3
Unresolved	<u>0.6</u>	<u>19.9</u>	<u>23.0</u>	<u>10.0</u>
Total	93.3	86.9	91.9	81.4

3) Analysis of Soil Treated with  $^{14}\text{C}$ -CGA-15324

Interval (Days)	0			14		
Depth (Inches)	<u>0-3</u>	<u>3-6</u>	<u>6-8</u>	<u>0-3</u>	<u>3-6</u>	<u>6-8</u>
Total ppm	0.952	0.022	0.043	0.729	0.020	0.013

<u>Balance in 0-3" Layer</u>	<u>Radioactive Distribution in Percent</u>	
Organic	42.1	23.8
Polar	4.2	3.4
Non-extractable	<u>53.7</u>	<u>87.7</u>
Total	100.0	114.9

Ionic Characterization  
of the 0-3" Extractables

Acids	6.6	7.2
Bases	1.1	.8
Neutrals	37.5	18.4
Zwitterions	<u>1.1</u>	<u>0.8</u>
Total	46.3	27.2

Conclusions

- 1) 4-Bromo-2-chlorophenol reached a level of 10% of the extractable activity from lettuce 21 days after treatment. Another 10% of the extractable activity remains unresolved at day 21. The activity found in the polar fraction is of an acidic nature (>80%) at all time intervals.
- 2) There was no significant leaching of soil activity, but the plant watering schedule was not submitted. Immediately after application to the soil, 53.7% of the activity became non-extractable which climbed to 87.7% at day 14. At day 0, 42.1% of the activity was extractable with organic solvents, but this dropped to 23.8% at day 14. Polar soluble products are not identified but most of the extractable activity is not in the form of parent.

3.3 Microbial Data

- 3.3.1 The Effects of 5, 25 and 125 ppm of CGA-15324 [0-(4-bromo-2-chlorophenoxy)-0-ethyl-5-propylphosphorothioate] and 5 and 25 ppm of 4-bromo-2-chlorophenol on soil microorganisms 2/15/78. D. C. Ercegovich. Volume 1 of 9. Acces. No. 096856, 3/3/78, 8F2057, p. 256.

Fourteen species of fungi were exposed to 5, 25, and 125 ppm of CGA-15324 and 5 and 25 ppm of 4-bromo-2-chlorophenol incorporated into potato dextrose agar. Cultures were incubated at 26°C and the rate of fungal growth was determined by measuring the mean radius of mycelial extension. The percent of growth



inhibition was calculated for 8 replicate plates by comparing them with a similar number of controls.

Nine species of bacteria were exposed to 5, 25, and 125 ppm of CGA and 5 and 25 ppm 4-bromo-2-chlorophenol in broth cultures. Bacterial cultures were incubated at varying temperatures as indicated in Table 1 and plated after appropriate intervals of growth.

While only two bacterial populations (*Bacillus spp.*) were inhibited significantly by CGA-15324, nearly all the fungal populations were inhibited.

Conclusion: This is an acceptable microbial effects study showing that CGA-15324 does inhibit microbial populations important to soil fertility. It should be noted, however, that this study conflicts with previously submitted microbial studies (see EC review 100-EUP-53, 2/1/77).

TABLE 2.--Effects of CGA-15324 and 4-Bromo-2-chlorophenol on Fungi in Potato Dextrose Agar Plate Tests

Fungus <sup>1</sup>	Mean mm of Radial Growth at Various Concentrations					
	CGA-15324	Bromochlorophenol				
	0	5	25	125	5	25
<i>Aspergillus flaschentraegeri</i> (9) (13)	15.4	12.0	12.9	9.1	11.1	5.0
	22.0	18.4	19.6	15.9	18.4	12.4
<i>Aspergillus fumigatus</i> (4) (6)	17.0	15.3	13.9	12.4	18.5	4.9
	30.6	27.1	24.3	21.4	33.6	14.5
<i>Aspergillus oryzae</i> (8) (13)	21.9	16.9	17.1	9.0	20.4	5.8
	36.7	30.1	30.3	17.6	35.0	12.5
<i>Chaetomium globosum</i> (5) (7)	27.8	12.6	5.3	3.1	24.1	16.3
	37.9	16.6	12.1	4.9	35.1	23.1
<i>Fusarium equiseti</i> (3) (7)	19.0	10.5	4.5	3.6	22.8	14.4
	43.0	29.3	7.8	43.0	43.0	43.0
<i>Fusarium solani</i> (3) (7)	18.1	14.1	13.4	12.0	16.3	11.5
	43.0	38.5	32.3	43.0	43.0	37.0

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<i>Humicola grisea</i> (6)	20.0	19.4	17.4	16.6	20.3	6.5
	27.6	26.4	25.5	22.5	27.0	10.6
<i>Myrothecium roridum</i> (5)	25.9	25.3	19.6	22.5	24.4	21.5
	39.5	34.5	32.0	31.4	37.1	32.8
<i>Penicillium chrysogenum</i> (8)	14.0	12.3	11.9	10.6	13.0	3.5
	21.8	21.0	20.4	18.0	21.8	12.3
<i>Penicillium notatum</i> (6)	13.6	12.0	11.0	10.3	13.5	7.3
	20.6	19.0	12.6	14.9	19.6	5.6
<i>Scopulariopsis brevicaulis</i> (3)	41.3	38.1	25.1	29.4	40.8	21.5
	12.8	7.9	7.6	7.0	9.0	3.0
<i>Scopulariopsis koningii</i> (7)	9.0	8.0	8.0	7.0	8.3	6.0
<i>Stachybotrys chartarum</i> (7)	43.0	43.0	43.0	43.0	43.0	43.0
<i>Trichoderma viride</i> (3)						

Numbers in parentheses are days of incubation after inoculation.

### 3.4 Field Soil Dissipation

#### 3.4.1 The Uptake and Metabolism of $^{14}\text{C}$ Ring Labeled Curacron in Field Grown Cotton and Distribution in Soil, report # ABR-78007, 8F2057, vol 3 of 9, acc #096858.

(Note: Only the portion of this study dealing with curacron distribution in soil is germane and is considered in this part of the review.)

One row of Mississippi field-grown cotton at the first open boll stage of development (16 weeks) and growing in a plot 3' x 16' was sprayed over the top with  $^{14}\text{C}$  ring labeled curacron in a 4E formulation at 1 lb. ai/A once a week for 6 weeks. The soil was a Bosket silt loam (28.4% sand, 52.0% silt, 19.6% clay, 1.6% OM, pH=6.8, CEC=16.1 meq/100 g, bulk density=1.4 g/cc).

Before and after each spraying and 30 days after the last spraying, random soil samples were taken to 9". The samples were screened to 2 mm, air dried and combusted for total radioactivity.

The accumulated rainfall during the 72-day study was 9.2 inches.

### Results

1) Characterization of Radioactivity Equivalent to <sup>14</sup>C-Curacron in Soil

Total ppm**	Spray No.*						Mature Cotton Final Harvest ***
	1	2	3	4	5	6	
	0-3"	0-3"	0-3"	0-3"	0-3"	0-3"	0-3" 3-6" 6-9"
Before spraying	<0.05	0.03	0.04	0.02	0.11	0.23	0.24 <0.05 <0.05
After spraying	0.06	0.36	0.06	0.05	0.18	0.57	- - -

\*Weekly spray schedule

\*\*Equivalent to <sup>14</sup>C-Curacron

\*\*\*Interval between last spray and final harvest, 30 days

- 2) The registrant claims no significant loss due to volatility during drying and screening of the soil.

### Conclusions

- 1) Although this study was run outdoors it does not allow us to predict the fate of curacron in the soil after being sprayed on cotton under actual use conditions for the following reasons.
  - a) The row of cotton plants was sprayed for the first time at 16 weeks after planting. At this time, the plant is large and the bolls are opening. This large plant would cover most, if not all, of the 3-foot wide plot and residues not sprayed on the target plant but reaching the soil outside the plot would be outside the sampling area and not analyzed.
  - b) Under actual use conditions, as stated on the label, the cotton plant is sprayed when the larvae appear, which is 4 - 8 weeks after planting (or earlier), when the plant is small exposing more of the ground to the curacron spray.
  - c) This study does not simulate skip row planting of cotton (plant 4 rows, skip 4 rows) where soil is exposed to spray.
  - d) We don't know how many cotton plants were planted per foot to determine if normal agricultural practices were followed. (Some plantings are done in a crowded manner leaving less soil exposed.)
- 2) The assertion made by the registrant in the study that less than 10% of the applied pesticide would reach the soil may be true when the spray is applied to a single row of large plants, but is not true when considering points 1 (a)-(d), above.
- 3) This study does not satisfy any of our data requirements.

- 3.4.2 Residue Report AG-A 3831 (Soil). B. E. Holt. Cameron County, Texas. Volume 2 of 9. Acces. No. 096857, 3/3/78. 8F2057, p. 152.

CGA-15324 (4EC) was applied broadcast at the rate of 0, 3, and 6 lbs. a.i./A to cotton as well as to the bare ground. The clay type soil, having a pH of 8.3 and CEC of 23.6 and moisture content of 11-19%, was sampled to depths of 0-6" and 6-12" at intervals of 0, 14, 40, and 60 days after application.

#### Conclusions

- 1) Sampling times should include pre-application, day of application, and immediately post-application for each single or multiple application. Identification of residues comprising more than 10% of initial application or 0.01 ppm, whichever is greater, is needed. Residues other than those hydrolyzable to the free phenol (BCP) are to be identified and this study does not reflect the recommended use pattern of multiple applications.
- 2) GC analyses of soil samples showed that total residue values determined as BCP (4-Bromo-2-chlorophenol) declined rapidly and could not be detected in any of the samples after 40 days of application.

- 3.4.3 Residue Report AG-A 3838 (Soil). W. Davidson. Fresno County, California. Volume 2 of 9. Acces. No. 096857, 3/3/78. 8F2057, p. 160.

CGA-15324 (4EC) was applied broadcast at the rate of 0, 3 and 6 lbs. a.i./A to a sandy loam soil having a pH of 7.1 CEC of 4.6, and moisture content of 3-11%. Soil samples were taken at depths of 0-6" and 6-12" at intervals of 0, 15, 30, 59, 119, and 240 days after application and analyzed by gas chromatography.

#### Conclusions

- 1) Sampling times should include pre-application, day of application, and immediately post-application for each single or multiple application. Identification of residues comprising more than 10% of

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initial application or 0.01 ppm, whichever is greater, is needed. The study does not reflect the recommended use pattern of multiple applications.

- 2) Residues in the 0-6" layer decreased more than 90% after the first 15 days and could not be measured in the 6-12" layer.

3.4.4 Residue Report AG-A 3903 (Soil). S. Moore. Washington County, Mississippi. Volume 2 of 9. Acces. No. 096857, 3/3/78. 8F2057, p. 170.

CGA-15324 (4EC) was applied broadcast at the rate of 0, 3, and 6 lb. a.i./A to a clay loam, having a pH of 7.0, CEC of 8.2 and moisture content of 11-17%. Soil samples were taken at depths of 0-6" and 6-12" at intervals of 0, 15, and 30 days after application and analyzed by gas chromatography.

Conclusions

- 1) Sampling times should include pre-application, day of application, and immediately post-application for each single or multiple application. Identification of residues comprising more than 10% of initial application of 0.01 ppm, whichever is greater, is needed. The study does not reflect the recommended use pattern of multiple applications.
- 2) Residues were not detectable (<0.05 ppm) after 15 days in all soil samples.

3.5 Rotational Crop Data

3.5.1 Uptake of the Soil Metabolites of  $\phi$ - $^{14}\text{C}$ -CGA-15324 by Rotation Corn Following Eight Weeks of Aging, ABR-78010, 8F2057 vol 3 of 9, acc #096858.

A 3'x16' plot of Bosket silt loam (28.4% sand, 52.0% silt, 19.6% clay, 1.6% OM, pH=6.8, cation exchange capacity=16.1 meq/100 g and bulk density=1.4 g/cc) was treated with  $^{14}\text{C}$  ring labeled curacron at 2 lb. ai/A pre-emergent to cotton. After 8 weeks, the cotton was harvested and the plot rototilled to 3 inches.



Two rows of corn 1 foot apart were planted in a 3'x3' subplot. Soil and corn samples were taken periodically and the total radioactivity determined by combustion. Soil aliquots were also extracted with methanol:water (9:1).

Between the planting of corn on May 27, 1977, and its harvest on October 17, 1977, there were about 17.2 inches of rainfall. This study took place in Washington County, Mississippi.

Results

TABLE 3.--Uptake of Radioactivity in Rotation Corn

	Weeks of Growth				
	5		15	20	
Plant part	Stalks	Stalks	Stalks	Cobs <sup>a</sup>	Grain <sup>a</sup>
Total ppm <sup>b</sup>	0.006	0.017	0.058	<0.008	<0.008

<sup>a</sup>Radioactivity in this sample was detected but too low for accurate quantitation in accordance with AG-276 (5).

<sup>b</sup>Equivalent to  $\phi$ -<sup>14</sup>C-Curacron.

TABLE 4.--Balance of Radioactivity in Soil Treated with  $\phi$ -<sup>14</sup>C-Curacron Used to Grow Rotation Corn

	Weeks after Treatment					
	8 (0)*			28 (20)*		
Depth (inches)	0-3	3-6	6-9	0-3	3-6	6-9
Total ppm**	0.21	0.01	<0.01	0.23	<0.01	<0.01

TABLE 4--Continued

<u>Balance</u>	<u>Percent of Total Radioactivity</u>
Extracted	8.5
Non- extractable	<u>85.0</u>
Total	93.5

\*Numbers in parentheses indicate the age of crop.

\*\*Equivalent to  $\phi$ - $^{14}\text{C}$ -Curacron.

Conclusions

- 1)  $^{14}\text{C}$  residues are taken up by rotation corn planted 8 weeks after application of 2 lb. ai/A of  $^{14}\text{C}$  curacron. Residues of 0.058 ppm equivalent to curacron were found in 20-week old corn stalks. Unidentifiable residues at  $<0.008$  ppm were found in the 20-week old cobs and grain.
- 2) Between planting and harvesting the corn, residues found in the soil remained constant at 0.21-0.23 ppm equivalent to curacron. Residues leaching past the 3" level were not greater than 0.01 ppm every 3 inches.
- 3) At planting of the corn (8 weeks after curacron application) 85% of the total soil residues were unextractable and 8.5% were extractable using methanol:water (9:1).
- 4) We note the label allows a maximum of 6 lb. ai/A and that residues in the soil remain constant at 0.2 ppm during the 28 weeks post-application of 2 lb. ai/A. This implies that greater uptake factors would have probably been realized if the maximum of 6 lb. ai/A was used to fortify the soil.

3.5.2 Uptake of the Soil Metabolites of  $\phi$ - $^{14}\text{C}$ -CGA-15324 by Rotation Lettuce following Twenty-three Weeks of Aging, ABR 78015, 8F2057, vol 3 of 9, acc #096858.

A 3'x16' plot of Bosket silt loam (28.4% sand, 52.0% silt, 19.6% clay, 1.6% OM, pH=6.8, cation exchange capacity=16.1 meq/100 gm and bulk density=1.4 gm/cc) was treated with  $^{14}\text{C}$  ring labeled curacron at 2 lb. ai/A pre-emergent to cotton. After 8 weeks, the cotton was harvested and the plot rototilled to 3 inches. The lettuce was planted in a 3'x3' subplot 23 weeks after treatment and was harvested 6 and 11 weeks after planting. Soil samples were taken at 0 and 11 weeks after planting.

Samples were combusted for determination of total radioactivity and the soil was additionally extracted with methanol:water (9:1).

Between the planting of lettuce on September 9, 1977, and its harvest on November 21, 1977, there were about 16.8 inches of rainfall. This study took place in Washington County, Mississippi.

### Results

TABLE 5.--Uptake of Radioactivity in Rotation Lettuce

	Weeks of Growth	
	6	11
Plant part	Leaves	Leaves
Total ppm <sup>b</sup>	0.012	<0.002 <sup>a</sup>

<sup>a</sup>Radioactivity in this sample was detected but too low for accurate quantitation in accordance with AG-276 (5).

<sup>b</sup>Equivalent to  $\phi$ - $^{14}\text{C}$ -Curacron.

TABLE 6.--Balance of Radioactivity in Soil Treated with  $\phi$ - $^{14}\text{C}$ -Curacron Used to Grow Rotation Lettuce

	Weeks After Treatment*					
	23 (0)			34 (11)		
Depth (inches)	0-3	3-6	6-9	0-3	3-6	6-9
Total ppm**	0.26	0.01	0.01	0.14	<0.01	<0.01
<u>Balance</u>	<u>Percent of Total Radioactivity</u>					
Extracted	5.7					
Non-extractable	<u>102.7</u>					
Total	108.4					

\*Numbers in parentheses indicate the age of crop.

\*\*Equivalent to  $\phi$ - $^{14}\text{C}$ -Curacron.

Conclusions

- 1) The interval before the planting of rotational lettuce, 23 weeks, is exceptionally long, but  $^{14}\text{C}$  residues of 0.26 ppm were still found in the top 3" of soil. Lettuce harvested at 6 weeks (29 weeks after curacron application) showed 0.012 ppm  $^{14}\text{C}$  residues in the leaves. At 11 weeks, this level dropped to <0.002 ppm.
- 2) At 34 weeks after curacron application, 0.014 ppm  $^{14}\text{C}$  residues were found in the top 3". Leaching past 3" at 23 and 34 weeks did not exceed 0.01 ppm.
- 3) At the time of lettuce planting, 5.7% of the soil activity was extractable and 102.7% was unextractable using methanol:water (9:1).
- 4) We note the label allows 6 lb. ai/A to be applied and although in this study only 2 lb. ai/A were

applied, 0.26 ppm were still in the soil at 23 weeks. This implies that greater uptake factors would have probably been realized if the maximum of 6 lb. ai/A was used to fortify the soil.

3.5.3 Uptake of the Soil Metabolites of  $\phi$ - $^{14}\text{C}$ -CGA-15324 by Rotation Soybeans Following Eight Weeks of Aging, ABR 78016, 8F2057 vol 3 of 9, acc #096858.

A 3'x16' plot of Bosket silt loam (28.4% sand, 52.0% silt, 19.6% clay, 1.6% OM, pH=6.8, cation exchange capacity=16.1 meq/100 gm and bulk density=1.4 gm/cc) was treated with  $^{14}\text{C}$  ring labeled curacron at 2 lb. ai/A pre-emergent to cotton. After 8 weeks, the cotton was harvested and the plot rototilled to 3 inches. The soybeans were planted in a 3'x3' subplot 8 weeks after treatment and were harvested 5, 15 and 20 weeks after planting. Soil samples were taken at 8 and 28 weeks after application of curacron.

Samples were combusted for determination of total radioactivity and the soil was additionally extracted with methanol:water (9:1).

Between the planting of soybeans on May 27, 1977, and their harvest on October 28, 1977, there were about 17.1 inches of rainfall. This study took place in Washington County, Mississippi.

TABLE 7.--Uptake of Radioactivity in Rotation Soybeans

	Weeks of Growth				
	5	15	20		
Plant growth	Stalks	Stalks	Stalks	Pods	Beans
Total ppm <sup>a</sup>	0.015	0.048	0.184	0.063	0.025

<sup>a</sup>Equivalent to  $\phi$ - $^{14}\text{C}$ -Curacron.

TABLE 8.--Balance of Radioactivity in Soil Treated with  $\phi$ - $^{14}\text{C}$ -Curacron Used to Grow Rotation Soybeans

	Weeks After Treatment*					
	8 (0)			28 (20)		
Depth (inches)	0-3	3-6	6-9	0-3	3-6	6-9
Total ppm**	0.11	<0.01	<0.01	0.16	<0.01	<0.01
<u>Balance</u>	<u>Percent of Total Radioactivity</u>					
Extracted	7.5					
Non-extractable	<u>98.7</u>					
Total	105.2					

\*Numbers in parentheses indicate the age of crop.

\*\*Equivalent to  $\phi$ - $^{14}\text{C}$ -Curacron.

### Conclusions

- 1)  $^{14}\text{C}$  residues of curacron are taken up by rotation soybeans planted 8 weeks after application of 2 lb. ai/A of  $^{14}\text{C}$ -curacron. At 20 weeks of growth, the stalks, pods and beans contained 0.184, 0.063 and 0.025 ppm residues (equivalent to curacron), respectively.
- 2) During the growth of the soybeans (week 8 through 28 after curacron application) residues in the top 3" were 0.11-0.16 ppm. Residues leaching past the 3" level were less than 0.01 ppm per 3" segment.
- 3) At planting of the soybeans, 7.5% of the activity was extractable and 98.7% was non-extractable from the soil.

4) We note the label allows a maximum of 6 lb. ai/A and that residues in the soil remain constant at 0.11-0.16 ppm during the growth of the soybeans (when only 2 lb. ai/A was applied 8 weeks before soybean planting). This implies that greater uptake factors would have probably been realized if the maximum of 6 lb. ai/A was used to fortify the soil.

3.5.4 Uptake of the Soil Metabolites of  $\phi$ - $^{14}\text{C}$ -CGA-15324 by Rotation Sugar Beets following Ten Weeks of Aging, ABR-78017, 8F2057, vol. 3 of 9, acc. #096858.

A 3'x16' plot of Bosket silt loam (28.4% sand, 52.0% silt, 19.6% clay, 1.6% OM, pH=6.8, cation exchange capacity=16.1 meq/100 bm and bulk density=1.4 gm/cc) was treated with  $^{14}\text{C}$  ring labeled curacron at 2 lb. ai/A pre-emergent to cotton. After 8 weeks, the cotton was harvested and the plot rototilled to 3". The sugar beets were planted in a 3'x3' subplot 8 weeks after the curacron application but had to be replanted 2 weeks later (at 10 weeks after curacron application). The sugar beets were harvested at 6, 18 and 24 weeks of growth and soil samples were taken at 10 and 34 weeks after curacron treatment.

Samples were combusted for determination of total radioactivity and the soil was additionally extracted with methanol:water (9:1).

Between the planting of sugar beets on June 6, 1977, and their harvest on November 21, 1977, there were 2.4 inches of rainfall. This study took place in Washington County, Mississippi.

TABLE 9.--Uptake of Radioactivity in Rotation Sugar Beets

Plant part	Weeks of Growth					
	6		18		24	
	Tops	Leaves <sup>a</sup>	Beets <sup>a</sup>	Leaves <sup>b</sup>	Beets <sup>b</sup>	
Total ppm <sup>c</sup>	0.029	<0.006*	<0.006*	<0.002	<0.002	

<sup>a</sup>Radioactivity in this sample was detected but too low for accurate quantitation in accordance with AG-276 (5).

<sup>b</sup>Radioactivity in this sample was below the limits of detection in accordance with AG-276 (5).

<sup>c</sup>Equivalent to  $\phi$ -<sup>14</sup>C-Curacron.

TABLE 10.--Balance of Radioactivity in Soil Treated with  $\phi$ -<sup>14</sup>C-Curacron Used to Grow Rotation Sugar Beets

Depth (inches)	Weeks after Treatment					
	8 (0)			34 (24)		
	0-3	3-6	6-9	0-3	3-6	6-9
Total ppm**	0.22	<0.01	0.01	0.18	<0.01	<0.01
<u>Balance</u>	<u>Percent of Total Radioactivity</u>					
Extracted	4.4					
Non-extractable	96.4					
Total	100.7					

\*Numbers in parentheses indicate the age of crop.

\*\*Equivalent to  $\phi$ -<sup>14</sup>C-Curacron.



### Conclusions

- 1)  $^{14}\text{C}$  residues are taken up by rotation sugar beets planted 10 weeks after application of 2 lb. ai/A  $^{14}\text{C}$  curacron to the soil. Residues of 0.029 ppm are found in the tops at 6 weeks but less than 0.006 ppm are found in the leaves or beets between 18 and 24 weeks.
- 2) Between planting and harvesting the sugar beets, residues found in the soil remained constant at 0.18-0.22 ppm equivalent to curacron. Residues leaching past the 3" level were not greater than 0.01 ppm every 3".
- 3) At planting of the sugar beets (10 weeks after curacron application), 4.4% of the soil activity was extractable with methanol:water (9:1) and 96.3% was unextractable.
- 4) We note the label allows a maximum of 6 lb. ai/A and that residues in the soil remain constant at about 0.2 ppm during the 24 weeks growth of the sugar beets after an application of only 2 lb. ai/A. This implies that greater uptake factors would have probably been realized if the maximum of 6 lb. ai/A was used to fortify the soil.

3.5.5 Uptake of the Soil Metabolites of  $\phi$ - $^{14}\text{C}$ -CGA-15324 by Rotation Spring Wheat Following Eight Weeks of Aging, ABR 78018, 8F2057 vol 3 of 9, acc #096858.

A 3'x16' plot of Bosket silt loam (28.4% sand, 52.0% silt, 19.6% clay, 1.6% OM, pH=6.8, cation exchange capacity=16.1 meq/100 gm and bulk density=1.4 gm/cc) was treated with  $^{14}\text{C}$  ring labeled curacron at 2 lb. ai/A pre-emergent to cotton. After 8 weeks, the cotton was harvested and the plot rototilled to 3". Spring wheat was planted in 3 rows 9" apart in a 3'x3' subplot.

Soil samples were taken at wheat planting and 20 weeks later and the wheat was sampled at 4, 10 and 14 weeks of growth.

Samples were combusted for determination of total radioactivity and the soil was additionally extracted with methanol:water (9:1).

Between the planting of wheat on May 27, 1977, and its harvest on September 13, 1977, there were about 10.1 inches of rainfall. This study took place in Washington County, Mississippi.

Results

TABLE 11.--Uptake of Radioactivity in Rotation Spring Wheat

Plant part	Weeks of Growth			
	4	10	14	
	Stalks	Stalks	Straw	Heads (Hulls & Grain)
Total ppm <sup>a</sup>	0.039	0.070	0.125	0.128

<sup>a</sup>Equivalent to  $\phi$ -<sup>14</sup>C-Curacron.

TABLE 12.--Balance of Radioactivity in Soil Treated with  $\phi$ -<sup>14</sup>C-Curacron Used to Grow Rotation Spring Wheat

Depth (inches)	Weeks after Treatment*					
	8 (0)			22 (14)		
Total ppm**	0-3	3-6	6-9	0-3	3-6	6-9
	0.24	0.01	0.01	0.15	<0.01	<0.01
Balance	Percent of Total Radioactivity					
Extracted	7.4					
Non-extractable	86.3					
Total	93.7					

\*Numbers in parentheses indicate the age of crop.

\*\*Equivalent to  $\phi$ -<sup>14</sup>C-Curacron.

### Conclusions

- 1)  $^{14}\text{C}$  residues are taken up by rotation wheat planted 8 weeks after application of 2 lb. ai/A of  $^{14}\text{C}$  curacron. Residues of 0.125 ppm were found in the straw and 0.128 ppm in the heads (hulls plus grain) at 14 weeks growth.
- 2) Between planting and harvesting the spring wheat, 8-22 weeks after application of 2 lb. ai/A  $^{14}\text{C}$  curacron,  $^{14}\text{C}$  residues in the top 3" of soil were 0.15-0.24 ppm. Leaching beyond 3" did not exceed 0.01 ppm per 3" segment.
- 3) At planting of the wheat (8 weeks after curacron application) 86.3% of the soil residues were non-extractable and 7.4% were extractable using methanol:water (9:1).
- 4) We note the label allows a maximum of 6 lb. ai/A and that at an application rate of 2 lb. ai/A, the  $^{14}\text{C}$  residues remain constant at about 0.2 ppm between 8 and 22 weeks after application. This implies that greater uptake factors would have probably been realized if the maximum of 6 lb. ai/A was used to fortify the soil.

#### 3.5.6 Residues in Pinto Beans, AG-A 4231 I, II

Curacron was sprayed foliar to cotton on September 26, October 1, 6, 11, 16, 21 in 1975 at 1 and 2 lb. ai/A per application. Pinto beans were planted May 4, 1976, and harvested July 1, 1976, as forage and September 23, 1976, as fodder and beans. These correspond to 252 and 315 day intervals between last treatment and harvest.

Extraction method AG-283 and AG-301 (modified) were used. Recoveries of 72-75% were realized. The soil was a sandy loam 55.2% sand, 34.8% silt, 10% clay, 1.3% OM, CEC=0.5 and pH=6.5.

### Results

Detectable residues (<0.05 ppm) were not found.

3.5.7 Residues in Sorghum, AG-A 4336

Curacron was sprayed foliar to cotton on July 9, 24, 28 and August 1, 6, 13 in 1975 at 1 and 2 lb. ai/A per application. Sorghum was planted April 21, 1976, and harvested July 22, 1976 (343 days after the last treatment).

Extraction method AG-283 and AG-301 were used for analysis. Recoveries of 100% were found. The soil was a clay of 41.2% sand, 16.8% silt, 42.0% clay, 1.7% OM, CEC=23.6 and pH=8.3. Recoveries were 100%.

(Two other sorghum rotational crop studies were run, but the registrant claims samples were contaminated by spray drift. Those 2 studies are not reviewed here and will not be considered with this evaluation.)

Results

Detectable residues (<0.05 ppm) were not found in sorghum forage.

3.5.8 Residues in Soubean Forage, AG-A 4369.

The registrant claims that soybean samples were contaminated by spray drift. The results, therefore, are invalid.

3.5.9 Residues in Winter Wheat, AG-A 4580 I, II and 4580 I, II, Second Report.

Curacron was sprayed foliar to cotton for 2 consecutive years on September 26, October 1, 6, 11, 16, 21 in 1975 and then on September 27, October 2, 7, 12, 17, 22 in 1976 at 1 and 2 lb. ai/A per application. Winter wheat was planted December 12, 1976, and harvested April 20, 1977, as forage and on June 8, 1977, as straw and grain. These correspond to 180 and 229 day intervals between last treatment and harvest.

Analysis was via methods AG-283 and AG-301. The soil was a sandy loam of 55.2% sand, 34.8% silt, 10.0% clay, 1.3% OM, CEC=0.5 and pH=6.5. Recoveries were 72-90%.

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### Results

Detectable residues (<0.05 ppm) were not found in winter wheat forage, straw or grain.

- 3.5.10 Residues in Spring Wheat, AG-4636, I, II and 4636, I, II, Second Report.

Curacron was sprayed foliar to cotton for 2 consecutive years on September 15, 25, 29 and October 2, 8, 12 in 1975 and on August 27, September 1, 6, 11, 16, 23 in 1976 at 1 and 2 lb. ai/A per application. Spring wheat was planted March 16, 1977, and sampled April 29, 1977, as forage and on June 21, 1977 as grain. These correspond to 219 and 271 day intervals between the last application and sampling.

Analysis was run using AG-283 and AG-301. Soil type and profile are not given. Recoveries were 86-91%.

### Results

Detectable residues (<0.05 ppm) were not found in spring wheat forage or grain.

- 3.5.11 CGA-15324: Analytical Methodology for Rotational Crops - Additional Information (ABR-78043) vol 1 of 1, acc. #233984, May 22, 1978.

Samples from the soybean and spring wheat <sup>14</sup>C-curacron rotational crop studies (3.5.3 and 3.5.5, above) were extracted via method AG-322 and with a separate base/acid reflux to determine if additional activity as 4-bromo-2-chlorophenol could be extracted with these 2 methods over previous extractions using AG-283.

The plant samples, due to freezer storage, lost water resulting in an increase in the ppm concentration of <sup>14</sup>C residues (see results below).

The soybeans and spring wheat were planted 8 weeks after application of 2 lb. ai/A of <sup>14</sup>C-curacron. Soybean forage samples were taken at 20 weeks of growth and wheat straw at 14 weeks of growth.

### Results

- 1) The initial  $^{14}\text{C}$  residue concentrations were 0.359 ppm in the soybean forage and 0.223 ppm in the wheat straw. (The freezer storage increased these values from 0.184 and 0.125 ppm, respectively.
- 2) AG-322 extracted a total of 19.7% and 18.4% of the  $^{14}\text{C}$  activity from the soybean forage and wheat straw, respectively. After subjecting this extracted activity to the basic and acidic refluxing and partitioning into isooctane and hexane, 4-bromo-2-chlorophenol (BCP) was not detected (<0.05 ppm) in the organic fraction.
- 3) The basic/acidic refluxing done directly to the soybean plant material extracted 71.9% of the total activity and hexane partitioning extracted 14.5% of the total activity into the hexane. No BCP (<0.05 ppm) was detected in the hexane fraction, but the identity of the hexane activity remaining and that in the aqueous layer was not identified.

### Conclusions

- 1) Curacron residues containing the 4-bromo-2-chlorophenol (BCP) moiety cannot be detected (<0.05 ppm) among the  $^{14}\text{C}$  residue taken up by rotational crops. Most probably, the ring moiety is being conjugated to natural products in the plant. However, 72% of these conjugated residues are released through basic/acidic refluxing done directly to the plant material and separate 4:1 in an aqueous:organic partition. Residues of BCP are not detected (<0.05 ppm) in the organic (hexane) fraction but the identity of the organic or aqueous activity is not given. We defer to the Toxicology Branch as to the significance of these residues.
- 2) Pending a decision from Toxicology Branch, there is no potential hazard to rotational crops from curacron usage.

### 3.6 Fish Accumulation

#### 3.6.1 Accumulation and Elimination of $^{14}\text{C}$ -Residues by Fish Exposed to $^{14}\text{C}$ -CGA-15324. Bionomics Lab 5/77 Ladd and Sleight. Volume 2 of 9 Acces. No. 096857, 3/3/78. 8F2057, p. 54.

The protocol for this experiment was similar to that in "Accumulation and Elimination of  $^{14}\text{C}$ -Residues by Bluegill Exposed to  $^{14}\text{C}$ -CGA-15324." Bionomics Lab. Barrows and Krasny (7/77) volume 1 or 9, p. 112. In this experiment bluegill sunfish were exposed to 30 ppb  $^{14}\text{C}$ -CGA-15324.

After 9 days of exposure, all the fish became dark in color, remained aggregated near the bottom of the aquarium, and exhibited "flashing" characteristic of chemical toxicity. Between days 7 and 9 of exposure, 2% mortality was observed. The study was terminated on day 9 and  $^{14}\text{C}$ -Residues in fish were reported.

TABLE 13.--Mean Measured  $^{14}\text{C}$ -residues, Calculated as CGA-15324, in Water and Bluegill Sunfish (*Lepomis macrochirus*) during 7 Days of Aqueous Exposure to a Nominal Concentration of 30  $\mu\text{g}/\ell$   $^{14}\text{C}$ -CGA-15324

Day	Conc. in Water	$^{14}\text{C}$ -residue Concentrations (mg/kg)		
		Heads	Carcasses	Viscera
1	21 (0) <sup>a</sup>	2.0 (0.3)	1.6 (0.1)	21 (6)
3	33 (1)	2.9 (1.3)	1.2 (0.8)	25 (10)
7	35 (0)	5.6 (0.0)	3.5 (0.1)	25 (10)

<sup>a</sup>Mean and standard deviation.

#### Conclusion

According to Fish and Wildlife, we can assume that carcasses include muscle tissue. Accumulation factors,

however, cannot be determined accurately since the fish died during the experiment. This experiment should be considered in conjunction with other fish accumulation and metabolism studies in Volume 1 of 9 pp. 112, 196. 207.

- 3.6.2 Accumulation and Elimination of  $^{14}\text{C}$ -Residues by Bluegill Exposed to  $^{14}\text{C}$ -CGA-15324. Bionomics Lab. Barrows and Krasny (7/77). Volume 1 of 9. Acces. No. 096856, 3/3/78. 8F2057, p. 112.

A modified, intermittent-flow, proportional diluter was used to deliver well water (pH of 7.1) into two glass aquaria (exposure and control aquaria). The system was calibrated to a turnover rate of 4 aquarium volumes per day.  $^{14}\text{C}$ -ring labeled CGA-15324 was added to the aquarium, resulting in a concentration of approximately 1 ppm. Bluegill sunfish were exposed to  $^{14}\text{C}$ -CGA-15324 for 28 days followed by 14 days depuration in flowing, uncontaminated water.

### Results



TABLE 14.--Mean Measured <sup>14</sup>C-residues, Calculated as CGA-15324, in Water and Bluegill Sunfish (*Lepomis macrochirus*) during 28 Days of Continuous Aqueous Exposure to a Nominal Concentration of 1.0 µg/l <sup>14</sup>C-CGA-15324 and during 14 Days of Depuration in Flowing, Uncontaminated Water

Day	Conc. in Water (µg/l)	<sup>14</sup> C-residue Concentrations (µg/kg)				Whole Body
		Muscle	Head	Viscera		
Exposure						
0	0.86 (0.02) <sup>a</sup>					
1	0.63 (0.03)	15.67 (5.31) <sup>b</sup>	16.37 (2.61) <sup>b</sup>	141 (43) <sup>c</sup>	22.30	1
3	0.82 (0.02)	14.50 (2.99)	22.27 (1.55)	285 (69)	34.89	3
7	0.91 (0.02)	12.80 (1.35)	39.23 (2.38)	394 (146)	44.74	1
10	1.02 (0.02)	12.97 (5.51)	30.37 (1.07)	297 (169)	39.91	
14	0.92 (0.01)	12.40 (4.33)	22.40 (3.38)	629 (108)	58.64	
21	1.02 (0.15)	17.27 (0.47)	36.53 (4.24)	396 (123)	55.93	
28	0.90 (0.00)	16.60 (0.44)	31.80 (6.84)	564 (245)	58.00	
Depuration						
1		1.68 (0.29)	5.55 (0.50)	411 (327)	35.06	
3		<1.32 (0.14) <sup>d</sup>	1.60 (0.08)	30.02 (14.11)	<4.17	

8	<1.23 (0.03)	<1.20 (0.03)	5.42 (1.23)	<1.62
10	<1.16 (0.04)	<1.43 (0.13)	7.55 (1.31)	<1.79
14	<1.19 (0.02)	<1.14 (0.12)	6.98 (1.52)	<1.67

a Mean and standard deviation based on the radiometric analyses of triplicate samples.

b Mean and standard deviation based on the radiometric analyses of three aliquots of the homogenized tissue from five fish.

c Mean and standard deviation based on the radiometric analyses of five visceral samples.

d Denotes all measured concentrations in a sample set were below minimum detectable limits.

### Conclusions

- 1) The results indicate that the concentration of  $^{14}\text{C}$ -residues in the water remained relatively constant ( $0.88 \pm 0.12$  ppm) throughout the exposure period. Radiometric analyses of the hexane extracts from water sampled weekly during exposure indicate that 30-55% of the  $^{14}\text{C}$ -residues present were extractable with hexane.
- 2)  $^{14}\text{C}$ -residues present in homogenized muscle tissue remained constant during the exposure period exhibiting a mean equilibrium bioconcentration factor of 17x. The mean concentration of  $^{14}\text{C}$ -residues measured in the head portion varied between 24-42x the mean concentration of  $^{14}\text{C}$ -CGA-15324 measured in the water. The visceral portion showed the largest pattern of uptake ranging from 320-676x the concentration of  $^{14}\text{C}$ -CGA-15324 measured in the water. Radiometric analyses of the whole fish showed a mean equilibrium bioconcentration factor of 60x.
- 3) Within 24 hours after transfer to uncontaminated water, bluegill had eliminated 90% and 83% of  $^{14}\text{C}$ -residues in the muscle and head portions measured on day 28 exposure. Within 72 hours after transfer, bluegill had eliminated 95% or more of  $^{14}\text{C}$ -residues in viscera and whole fish.
- 4) The identity of residues in water, whole body fish, edible tissue, and viscera were not determined. Accumulation factors reached 17x in the muscle tissue, 42x in the head, 676x in the viscera and 60x in the whole fish. This flow-through study should be considered in conjunction with Report Nos. ABR-77052 and ABR-77076 and a previously reviewed-static system.

3.6.3 The Metabolism of  $\phi$ - $^{14}\text{C}$ -CGA-15324 in Bluegill Fish. M12-130-4F. Report No. ABR-77076. Cargile and Cassidy (8/3/77). Volume 1 of 9. Acces. No. 096856, 3/3/78, 8F2057.

Bluegill fingerlings were exposed to 1 ppb of  $\phi$ - $^{14}\text{C}$ -CGA-15324 in a dynamic flow aquatic system for 28

days. Fish were harvested after 1, 3, 7, 14, 21 and 28 days of exposure and after 1, 3, 8, and 14 days of depuration. Water and fish samples were analyzed in the same manner as in Report No. ABR-77052. "The Metabolism of  $\phi$ - $^{14}\text{C}$ -CGA-15324 in Fish M2-130-3F."

Results

Uptake of  $^{14}\text{C}$  in all tissues reached a plateau by the seventh day of exposure. The greatest rate of bioaccumulation was in the viscera, resulting in levels of 400-500x while that in head and body was 10-40x. After removal from the pesticide, the fish lost 90% of radioactivity in all tissues.

There was insufficient radioactivity and sample to identify all metabolites. Less than 5% of the total  $^{14}\text{C}$  in the aqueous portion was parent compound and 33-48% was 4-bromo-2-chlorophenol.

TLC analysis of water samples from 15th and 21st days of exposure indicated 40-60% of the total radioactivity was parent, 15% was 4-bromo-2-chlorophenol sulfate. Water samples taken on the 28th day of exposure had about 30% parent and 55% 4-bromo-2-chlorophenol.

TABLE 15.--Total  $^{14}\text{C}$  Tissue Retention by Bluegills during Exposure to 1 ppb  $\phi$ - $^{14}\text{C}$ -CGA-15324 in Water

Days of Exposure	Water, ppb**	Tissue Retention in ppb*		
		Body	Viscera	Head
1	0.6	9	136	18
7	0.9	15	437	24
14	0.9	12	439	25
21	1.0	25	409	38
28	0.9	18	580	34
<u>Days of Depuration</u>				
8		1	7	2
14		1	--	2

TABLE 16.--Distribution of Radioactivity Found after Extraction of Fish Viscera

Days of Exposure	% of Total $^{14}\text{C}$		
	Organic	Aqueous	Nonextractable
1	71	34	4
7	56	33	5
14	51	25	9
21	62	32	2
28	43	61	4

### Conclusion

This report in conjunction with Report No. ABR-77052 and Bionomics Study, "Accumulation and Elimination of  $^{14}\text{C}$ -residues by Bluegill Exposed to  $^{14}\text{C}$ -CGA-15324" is acceptable. Bioaccumulation factors varied from 400-500x in viscera and 10-40x in head and whole body.

3.6.4 The Metabolism of  $\phi$ - $^{14}\text{C}$ -CGA-15324 in Fish. M2-130-3F. Report No. ABR-77052. Cargile and Cassidy (5/9/77) Volume 1 of 9. Acces. No. 096856, 3/3/78 8F2057.

Bluegill fingerlings were placed in a dynamic flow aquatic system containing 0.03 ppm  $\phi$ - $^{14}\text{C}$ -CGA-15324 (U-ring-labeled) and having four turnovers per day. Fish were harvested after 1, 3 and 9 days of exposure, divided into head, body and viscera, frozen and later analyzed for total radioactivity in tissues as well as characterization of metabolites.

Total radioactivity in tissues was determined by grinding the fish bodies and heads with dry ice and viscera with liquid nitrogen. Aliquots were combusted in a biological oxidizer.

TABLE 18.--Characterization of Metabolites in Fish Tissues during Exposure to 0.03 ppm  $\phi$ - $^{14}\text{C}$ -CGA-15324 in Water

	% of Total $^{14}\text{C}$					
	Viscera			Body		
	Days of Exposure					
	1	3	9	1	3	9
CGA-15324	19	7.6	28	22	33	62
4-bromo-2-chlorophenol	33	22	14	9.3	12	12
Polar unknowns	28	27	16	**	10	0.6
	ppm*					
CGA-15324	4.3	3.2	16	0.3	0.9	2.3
4-bromo-2-chlorophenol	7.6	9.0	8.2	0.1	0.3	0.5
Polar unknowns	6.3	11.5	8.8	**	0.3	**

\*Expressed as  $\phi$ - $^{14}\text{C}$ -CGA-15324

\*\*Too low to quantitate

There were four unknown polar metabolites representing 16% and 0.6% in viscera and body, respectively. Two of these compounds were thought to be 0-(4-bromo-2-chlorophenyl)-0-ethylphosphate and 4-bromo-2-chlorophenol sulfate.

Conclusion

This study in conjunction with Bionomics study "Accumulation and Elimination of  $^{14}\text{C}$ -residues by Blue-gill Exposed to  $^{14}\text{C}$ -CGA-15324" is acceptable. Bio-accumulation levels were as high as 1900x in viscera, 230x in the head and 120x in whole body.

3.7 Tank Mix Data

3.7.1 Residue Report AG-A 4108 (Soil). V. Seim. Vero Beach, Florida. Volume 2 of 9. Acces. No. 096857, 3/3/78. 8F2057, p. 191

This is a tank mix study in which 4.5 lbs. a.i./A CGA-15324 was hand-applied alone and in combination with 6.0 lbs. a.i./A chlordimeform and with 3.0 lbs. a.i./A azinphosmethyl to a sandy loam and silt loam maintained at 60-80% field capacity (pH 6.8 and 6.3, respectively). Two 6-inch core samples were analyzed by GC at intervals of 1, 15, and 30 days.

Results

CGA-15324

16ai/A	Application Date(s)	Sample Date(s)	Interval (Days)	Sand	Silt
0	Check	5/20/76		<0.10	<0.10
		6/3/76		<0.10	<0.10
		6/18/76		<0.10	-
4.5	CGA 15324	5/20/76	1	1.3	0.12
		6/3/76	15	0.44	<0.10
		6/18/76	30	0.27	-
6.0	Chlordimeform +	5/20/76	1	1.5	0.23
+4.5	CGA-15324	6/3/76	15	0.29	<0.10
		6/18/76	30	0.21	-
6.0	Chlordimeform +	5/20/76	1	1.3	0.33
+4.5	CGA-15324 +	6/3/76	15	0.32	<0.10
+3.0	Azinphosmethyl	6/18/76	30	0.17	-



Conclusions

- 1) Curacron degrades with a halflife of less than 2 weeks when applied alone or tank mixed with Guthion.
- 2) This is an acceptable tank mix study.

3.7.2 Residue Report AG-A 4635 (Soil). J. Thomas, Delta Research Farm. Washington, Mississippi. Volume 2 of 9. Acces. No. 096857, 3/3/78. 8F2057, p. 301.

Curacron 4E and methyl parathion 4E were applied individually and in tank mixtures at the rate of 6 + 3 lb. a.i./A to a silt loam (pH 6.6, CEC 13.9 and 1.1% organic matter). Tolban 4E was applied to the soil 3 days prior to the experiment at 1 lb. a.i./A while cotoran 80W was applied at 2 lbs. a.i./A right after planting cotton. Soil samples were taken at 6 inches on 0, 30, and 60 days post-treatment and analyzed by gas chromatography. Dissipation rates of curacron alone and in combination with methyl parathion are comparable.

Compound	Rate (lb. a.i./A)	Interval (days)	Residue (ppm)	
			CGA-15324	Methyl parathion
Curacron + methyl parathion	6 + 3	0	0.68	0.85
		30	<0.05	<0.05
		60	<0.05	<0.05
Curacron alone	6	0	0.96	-
		30	<0.05	-
		60	<0.05	-
Methyl parathion alone	3	0	-	0.65
		30	-	<0.05
		60	-	<0.05

Conclusion

Increased soil persistence of curacron is not expected when applied as a tank mix with methyl parathion.

3.7.3 Residue Report AG-A 5023 (Soil). S. Dumford. Lee, AL. Volume 2 of 9. Acces. No. 096857, 3/3/78. 8F2057, p. 319.

Curacron 6E and methyl parathion 4E were applied individually and in tank mixtures at the rate of 6 + 3 lb. a.i./A to a loamy sand (pH 6.3, CEC 6.6 and 1.2% organic matter). Soil samples were taken at a depth of 6 inches on 0, 31, and 62 days post-treatment and analyzed by gas chromatography. Dissipation rates of curacron alone and in combination with methyl parathion are comparable.

Compound	Rate (lb. a.i./A)	Interval (days)	Residue (ppm)	
			CGA-15324	Methyl parathion
Curacron + methyl parathion	6 + 3	0	1.4	0.55
		31	<0.05	<0.05
		62	<0.05	<0.05
Curacron alone	6	0	1.3	-
		31	0.06	-
		62	<0.05	-
Methyl parathion alone	3	0	-	0.46
		31	-	<0.05
		62	-	<0.05

Conclusion

Increased soil persistence of curacron is not expected when applied as a tank mix with methyl parathion.

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### 3.8 Analytical Methods

#### 3.8.1 Two Dimensional Thin Layer Chromatographic Separation of CGA-15324 and Some of Its Analogs, AG-270, 8F2057, vol. 1 of 9, acc. #096856.

This is a TLC technique for the identification of curacron and its degradation products when  $^{14}\text{C}$  labeled parent is used.

Silica gel plates are used and the two solvent systems are benzene:chloroform:ethyl acetate (40:40:20) and benzene. Visualization is via UV light followed by scraping and liquid scintillation counting.

This method will separate the parent as one spot and 4-bromo-2-chlorophenol as a second spot from the origin containing (4-bromo-2-chlorophenyl) phosphate and 0-(4-bromo-2-chlorophenyl)-5-n-propyl-sodium phosphorothioate and (4-bromo-2-chlorophenyl) ethyl sodium phosphate.

#### 3.8.2 Biphasic Extraction of Radioactive Metabolites from Treated Biological Material, AG-214, 8F2057, vol. 1 of 9, acc. #096856.

This is a procedure for the extraction of organic soluble and water soluble metabolites of  $^{14}\text{C}$  labeled materials from treated animal and plant tissues. The extractions are run in sequence and the procedures are taken from the literature.

Recovery data was not submitted.

#### 3.8.3 Radioassay of $^{14}\text{C}$ in Biological Materials by Combustion. Using the Harvey Biological Material Oxidizer (BMO), AG-252, 8F2057, vol. 1 of 9, acc. #09856.

Wet and dry feces, blood, plant and animal tissues containing  $^{14}\text{C}$  material are combusted, the  $^{14}\text{CO}_2$  trapped in liquid scintillation cocktail and counted in a liquid scintillation spectrometer.

Six combustions of 100 ul of  $^{14}\text{C}$  benzoic acid in 200 ul of control rat blood gave recoveries that ranged from 94.9-98.4%.

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3.8.4 Analytical Method - Gas Chromatographic Method for Assaying Residues of CGA-15324 in Soil Determined as 4-Bromo-2-chlorophenol, AG-301, 8F2057, vol. 2 of 9, acc. #096857.

A soil sample is extracted with 90% methanol, filtered and the filtrate made basic with NaOH, refluxed and then made acidic with HCl and refluxed. Next is partitioning with organic solvents which are then cleaned up, concentrated and analyzed for curacron determined as 4-bromo-2-chlorophenol ~~via~~ GC with an EC detector.   
via

Recovery for samples fortified with 0.1-2.0 ppm curacron averaged 89±13% (n=6).

Conclusions

This method is useful only in determining parent curacron and degradation products of curacron containing the intact 4-bromo-2-chlorophenyl moiety.

The sole use of this method cannot be relied upon to provide quantitative results or a material balance.

3.8.5 Determination of CGA-15324 in Plant Material by Gas Chromatography, AG-282, 8F2057, vol. 3 of 9, acc. #096858.

Green plant material is extracted with methanol and dry plant material is extracted with methanol:water (9:1). The extract is evaporated to a suspension and partitioned between benzene and sodium chloride solution.

The benzene fraction is analyzed by gas chromatography using a phosphorus specific flame photometric (526 nm) detector or an electron capture detector.

The limit of detection is 0.05 ppm and recovery is 50-112% for fortification levels of 0.05-3.0 ppm for various crops.

This method is a modification of REM 28/73.

- 3.8.6 High Voltage Electrophoresis for Characterization of Charged Radioactive Metabolites, AG-300, 8F2057, vol. 3 of 9, acc. #096858.

This is an electrophoresis method for separating degradation products of curacron. If radiolabeled material is being separated, then the electrophoresis paper can be cut into sections and combusted for quantitation.

Recovery data was not submitted.

- 3.8.6 Ion Exchange Characterization of Metabolites of Radioactive Pesticides, AG-156, 8F2057, vol. 5 of 6, acc. #096854.

This method is based on the fact that a cationic resin will exchange hydrogen ions for bases (+) and zwitterions ( $\pm$ ), letting acids (-) and neutrals (0) pass; that an anionic resin will exchange formate ions for acids (-) and zwitterions ( $\pm$ ) letting bases (+) and neutrals (0) pass; and that a double bed of the two resins will exchange hydrogen and formate for acids (-), bases (+), and zwitterions ( $\pm$ ) letting neutrals (0) pass.

Tests run on standard compounds, not including curacron and its metabolites, showed 93.6-100.0% recoveries.

- 3.8.8 Radioassay of  $C^{14}O_2$  by Acid Neutralization and Subsequent Counting by Liquid Scintillation, AG-250, 8F2057, vol. 5 of 6, acc. #096854.

Animal expired radioactive  $CO_2$  is passed through NaOH. The resultant carbonate is treated with acid and the liberated  $^{14}CO_2$  is absorbed in phenethylamine-water which is counted directly in Instagel. A parallel determination of the carbonate present in the NaOH is done by titration.

- 3.8.9 Extraction of Humic Acid and Fulvic Acid Fractions from Soil Containing Non-extractable  $^{14}C$ -residues, AG-268; 8F2057, vol. 5 of 6, acc. #096854.

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After extracting the soil with methanol/water (or other polar solvents), humic acid is extracted with NaOH and precipitated with HCl. The supernatant is partitioned with methylene chloride to remove the fulvic acid.

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- 3.8.10 Extraction of CGA-10832 Residues from Soil, AG-254, 8F2057, vol. 3 of 9, acc. #096858.

A soil aliquot is extracted with a methanol/water mixture (9:1 V/V) and the extract assayed via liquid scintillation techniques. An aliquot from the extract is partitioned between chloroform and the methanol/water and the chloroform layer assayed by liquid scintillation techniques.

The soil residue is combusted to determine activity remaining in the soil.

- 3.8.11 Blending of Soils and Homogenization of Biological Materials for Radioassay and Extraction, AG-223, 8F2057, vol. 3 of 9, acc. #096858.

Soils, feces, plant material or animal tissues are ground with dry ice and stored for later assay.

- 3.8.12 Gas Chromatographic Method for Assaying Residues of CGA-15324 in Cottonseed Determined as 4-Bromo-2-chlorophenol, AG-283, vol. 5 of 6, 8F2057, acc. #096854, p. 73.

The sample is blended with 90% MeOH and filtered. The extract is subjected to acidic; then basic refluxing and then partitioned into isooctane and a second partitioning into hexane. Following silica gel column clean-up and concentration, analysis is ~~via~~ GC/EC.

via

- 3.8.13 Gas Chromatographic Method for Assaying Residues of CGA-15324 in Cottonseed Determined as CGA-55960, AG-322, vol. 5 of 6, 8F2057, acc. #096854, p. 146.

This method replaces AG-283.

The sample is refluxed with 90% MeOH and filtered. The extract is subjected to basic then acidic

refluxing, then partitioned into isooctane and a second partitioning into hexane. Following silica gel column clean-up and concentration, analysis is via GC-EC.

### 3.9 Ancillary Data

#### 3.9.1 CGA-15324: Update of Environmental Impact Statement, ABR-78023, 8F2057, vol. 1 of 9, acc. #096856.

This is a registrant produced summary of the environmental chemistry data and it will not be evaluated in this review. However, each individual study comprising the summary will be addressed in this review.

— CGA-15324: Environmental Impact Statement, ABR-76048, 8F2057, vol. 1 of 9, acc. #096856.

This is a summary of some submitted studies and will not be evaluated in this review. However, each individual study will be addressed herein.

— Response to EPA: Summary of CGA-15324 Rotational Crop Data, ABR-77022, 8F2057, vol. 1 of 9, acc. #096856.

This report summarizes some rotational crop studies but will not be evaluated here. Rather, each individual rotational crop study will be addressed.

#### 3.9.2 Behavior of CGA-15324 on Cotton Leaf Surfaces, project report 52/77, 8F2057, vol. 1 of 9, acc. #096856.

Excised cotton leaves (about 50 cm<sup>2</sup> each) from 4 week old cotton plants were sprayed with a 1% active formulation of <sup>14</sup>C curacron via a single droplet generator. This rate simulated an aerial LV application of 750 gm ai/ha in 30 l of water or 11 droplets/cm<sup>2</sup> (0.67 lb. ai/A). The petioles of the leaves were kept in tap water.

One set of leaves was kept in a closed system so the volatile activity could be trapped and another set was kept in an open system.

Immediately after and at 1, 4, 24 and 96 hours post-treatment leaves were sampled, rinsed with hexane, then macerated and extracted with methanol (80%). Non-extractable activity was determined by combustion and the extractable activity was analyzed by TLC.

### Results

- 1) % residues profile after application to cotton leaves in closed system.

<u>Time (hours)</u>	<u>Surface</u>	<u>Subsurface</u>	<u>Metabolites</u>	<u>Volatiles</u>
1	95	4	0	0
4	87	11	1	3
24	66	23	3	9
96	20	48	7	25

- 2) % residues profile after application to cotton leaves in open system.

<u>Time (hours)</u>	<u>Surface</u>	<u>Subsurface</u>	<u>Metabolites</u>	<u>Volatiles (calculated)</u>
1	95	4	0	1
4	90	7	1	4
24	58	28	4	10
96	32	40	8	20

- 3) Surface and volatile activity was unchanged curacron at all time intervals. The activity in the leaf extract was primarily parent with small amounts of water soluble degradation products.

### Conclusions

At 4 day post-application to cotton leaf surfaces, volatile curacron residues would represent 20-25% of



the applied with 40-48% going beneath the leaf surface and 20-32% remaining on the leaf surface. Curacron would not degrade except for a small part of that fraction that was found subsurface to the leaf.

The above conclusions are drawn from a laboratory study. Under field conditions greater volatility, degradation and loss from the leaf surface (to the soil via rain water) would be expected.

3.9.3 Volatilization of CGA-15324 from Soil under Laboratory Conditions, project report 15/77, 8F2057, vol. 1 of 9, acc. #096856.

A Swiss and German soil were fortified with  $^{14}\text{C}$  curacron to 20, 40, 60 and 80 ppm, mixed and placed in a closed chamber (surface area  $48\text{ cm}^2$ , volume  $340\text{ cm}^3$ ) over which moisture saturated air passed. The outgoing air passed through ethylene glycol for capture of volatized curacron residues. The system was maintained at  $35^\circ\text{C}$ .

Samples of the ethylene glycol trapping solution were extracted with diethyl ether and sodium chloride solution. The ether was dried and analyzed by GC using  $\text{Ni}^{63}\text{EC}$  detector.

Profiles of the soils used are below:

Origin	pH	Organic Matter (%)	Water Capacity (%)	Mechanical Analysis		
				Clay (%)	Silt (%)	Sand (%)
Collombey VS, Switzerland	7.8	2.2	22	2.8	10.2	87.0
Hatzenbühl, Germany	4.8	1.8	20	10.5	12.4	77.1

The soils were initially brought to 12% soil moisture.

Results

1) Volatilization of CGA-15324 from a Sandy Soil (Collombey) at 12% Soil Moisture, an Air Flow Rate of  $30 \text{ l}\cdot\text{h}^{-1}$ , a Temperature of  $35^\circ\text{C}$  and a Sampling Period of 24 h.

Initial Soil Concentration* ( $\mu\text{g}\cdot\text{g}^{-1}$ )	Volatilization Rate			
	Total $^{14}\text{C}$ -activity ( $\text{ng}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ )	CGA-15324 ( $\text{ng}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ )	(%)	4-bromo-2-chlorophenol ( $\text{ng}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ ) (%)
20	27	3.1	11.5	21 77.8
40	54	5.5	10.2	45 83.3
60	74	6.8	9.2	60 81.1
80	104	9.5	9.1	86 82.7

\*On a wet soil-weight basis.

2) The only results reported for the Hatzenbühl sandy loam are 20% of the total volatilized activity was determined to be parent curacron.

### Conclusions

This study shows 0.13% of the initial fortification activity volatilizing per hour. Over a period of 24 hours, this will amount to 3% and to 21% over a week.

However, this study was run only 24 hours and the top soil layer would lose activity the quickest. Therefore, with time, volatilized activity will decrease and the values reported in this study are taken as minimal.

This study also shows 10% and 80% of the volatilized activity to be parent curacron and 4-bromo-2-chlorophenol, respectively, as volatilizing from the Col-lombey sand.

Volatility will be a significant vehicle for dissipation of curacron and the curacron degradation product 4-bromo-2-chlorophenol when applied in the field.

- 3.9.4 Metabolism and Balance Study of  $\phi$ - $^{14}\text{C}$ -CGA-15324 in a Lactating Goat. M11-130-1A. Report No. GAAC-76024. Thomas and Cassidy 4/7/76. The Identification of a Major Urinary Metabolite from a Goat Given  $\phi$ - $^{14}\text{C}$ -CGA-15324. M5-130-14A. Report No. ABR-76088. Simoneaux and Cassidy (12/17/76). Volume 3 of 6. Acces. No. 096852, 3/3/78, pp. 100 and 122.

The urinary excreta from a goat administered  $\phi$ - $^{14}\text{C}$ -CGA-15324 at a level of 5 ppm in the diet accounted for 85.4% of the dose (feces contained 4.4% and intestines 5.8% of the total dose). The structure of 87% of the urinary radioactivity was identified as the sulfate conjugate of 4-bromo-2-chlorophenol based upon electrophoretic behavior, enzyme analysis with aryl sulfatase and cochromatography on TLC.

Percent Recovery of Radioactivity from Goats Given  
 $\phi$ -<sup>14</sup>C-CGA-15324 for Nine Consecutive Days

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	% of Total Dose Ingested
Urine	85.0
Feces	4.4
Milk	0.1
CO <sub>2</sub> and volatiles	1.0
Blood	0.6
Tissues	0.9
Rumen and intestinal contents	5.8
Total	97.8

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Conclusion.

These are ancillary studies.

- 3.9.5 Distribution, Degradation and Excretion of CGA-15324 in the Rat. P.R. No. 16/74. U. Ifflaender 12/31/74. Volume 3 of 6. Acces. No. 096852, 3/3/78, p. 141.

The rate and route of excretion of CGA-15324 and the level of residues on tissues were determined in male and female rats after a single oral dose of 5 mg/kg randomly <sup>14</sup>C-ring labeled CGA-15324. The majority of the radioactivity was excreted in the urine (82-96%) with increasing amounts of 4-bromo-2-chlorophenol being formed with time. Parent compound was not detected in urine samples.

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Tissue	Tissue Residues (mean ± SEM) (in ppm CGA-15324 equivalents)	
	Males (n = 4)	Females (n = 3)
Liver	0.013±0.001	0.023±(0.007)
Fat	<L <sub>D</sub>	<L <sub>D</sub>
Kidney	0.007+0.001	0.008+(0.001)
Muscle	<L <sub>D</sub>	<L <sub>D</sub>
Blood	*	*
Testis	<L <sub>D</sub>	---
Ovary	---	<L <sub>D</sub>
Brain	<L <sub>D</sub>	<L <sub>D</sub>

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TABLE 19.--Excretion of Radioactivity by Rats after an Oral Dose of Approximately 5 mg/kg  $^{14}\text{C}$ -CGA-15324

	Excretion (mean $\pm$ SEM) (% of dose)	
	Males (n=4)	Females (n=3)
<b>Urine</b>		
0 - 24 hours	78.09 $\pm$ 8.83	91.37 $\pm$ (5.24)
24 - 48 hours	2.66 $\pm$ 0.53	3.46 $\pm$ (3.96)
48 - 72 hours	0.51 $\pm$ 0.24	0.51 $\pm$ (0.68)
72 - 144 hours	0.48	0.39
Subtotal	81.75 $\pm$ 9.34	96.40 $\pm$ (3.82)
<b>Faeces</b>		
0 - 24 hours	14.37 $\pm$ 7.74	1.14 $\pm$ (0.93)
24 - 48 hours	0.92 $\pm$ 0.22	0.65 $\pm$ (0.65)
48 - 72 hours	0.16 $\pm$ 0.03	0.16 $\pm$ (0.05)
72 - 144 hours	0.20	0.54
Subtotal	15.67 $\pm$ 7.97	2.47 $\pm$ (1.44)
Expired Air* 0 - 144 hours	0.08	0.07
Total Excretion	97.46 $\pm$ 1.37	98.89 $\pm$ (2.92)
Tissue Residues**	0.06 $\pm$ 0.02	0.05 $\pm$ (0.01)
Cage Wash	0.96 $\pm$ 0.38	1.71 $\pm$ (2.24)
Total Recovery	98.48 $\pm$ 1.14	100.65 $\pm$ (0.96)
Excretion half life time (hours)	<8	<8

\*Collected from two animals of each sex only.

\*\*Calculated from Table II assuming that fat, blood and muscle represent 14%, 6% and 38% of the body weight, respectively.

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Conclusion

This is an ancillary study.

- 3.9.6 CGA-15324. Dislodgeable Residues on Cotton, Chemonics Project 76-127, 8F2057, vol. 2 of 9, acc. #096857.

Cotton, of an unspecified age, growing in 3 plots of 0.466 acres each, was treated with curacron at 0, 1 and 2 lb. ai/A/application eight times between September 4 and November 3, 1976.

Samples of leaf discs 1.8 cm in diameter were taken with a leaf punch just before the November 3, 1976, application and at 0, 24, 48, 96 and 120 hours post application.

The whole leaf discs were extracted with hexane and the extract analyzed via GC (AG-282, reviewed in this evaluation).

The test took place 5 miles west of Phoenix, Maricopa County, Arizona. Between the first application and the last leaf disc sampling there were about 2.2 inches of rainfall.

Results

1) Residues of CGA-15324 Expressed in Parts per Million Following Application by Ground Equipment, Phoenix, Arizona, November 3, 1976

	Untreated Control			1.0 lb. Rate			2.0 lb. Rate		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Pre-treatment	0.08	0.08	0.09	3.75	5.25	6.25	3.93	4.05	4.23
0 hr. Post-treatment	0.27	0.32	0.77	33.84	34.61	44.07	75.62	80.08	81.52
24 hr. Post-treatment	0.21	0.32	0.39	13.09	15.00	16.41	23.44	27.87	32.31
48 hr. Post-treatment	0.16	0.19	0.33	8.98	9.85	11.76	16.92	21.01	26.43
72 hr. Post-treatment	0.17	0.22	0.24	7.57	8.95	9.29	15.49	18.94	19.03
96 hr. Post-treatment	0.08	0.09	0.09	7.77	8.75	8.98	13.43	13.71	15.72
120 hr. Post-treatment	0.08	0.08	0.08	7.58	8.86	9.37	11.15	12.31	15.07



2) Residues of CGA-15324 Expressed as mg/m<sup>2</sup> of Cotton Leaf Following Application by Ground Equipment, Phoenix, Arizona, November 3, 1976

	Untreated Control			1.0 lb. Rate			2.0 lb. Rate		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Pre-treatment	0.02	0.02	0.02	0.98	1.59	1.73	1.03	1.13	1.13
0 hr. Post-treatment	0.10	0.10	0.20	8.25	8.44	9.75	22.97	19.22	21.09
24 hr. Post-treatment	0.05	0.08	0.10	3.09	3.66	3.94	5.63	6.38	7.88
48 hr. Post-treatment	0.03	0.04	0.07	2.16	2.44	3.00	4.13	5.44	6.94
72 hr. Post-treatment	0.04	0.05	0.05	2.02	2.48	2.58	4.13	4.69	4.78
96 hr. Post-treatment	0.02	0.02	0.02	1.92	1.97	2.16	3.38	3.19	3.66
120 hr. Post-treatment	0.04	0.05	0.06	1.88	2.23	2.39	2.72	3.28	3.84

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## Conclusions

- 1) Dislodgeable residues of 7.6-9.4 ppm (1.88- 2.39 mg/m<sup>2</sup>) are released from cotton leaves after a hexane wash 120 hours after the last of 8 l lb. ai/A applications. The 8 applications were made over a 2 month period. Dislodgeable residues of 11.2-15.1 ppm (2.72-3.84 mg/m<sup>2</sup>) were released from 2 lb. ai/A application rate test.
- 2) Since hexane was used to wash the leaves and not water, the residues released are high. However, residues released from a water wash would be low since under actual field conditions during field entry, leaves are broken as evidenced by the "green stains" on clothing after leaving the field. So residues actually dislodgeable and available for pick up are a combination of those from the leaf surface and subsurface.

## 4.0 Summary

### 4.1 Hydrolysis

Curacron degrades more rapidly at basic pH's and increasing temperature. Halflives at 30°C at pH's 5, 7 and 9 are 670, 120 and 2 hours, respectively. Hydrolysis in basic solution is rapid yielding the 4-bromo-2-chlorophenol (CGA-55960 or BCP) and in acidic solution the following intermediates to BCP formation are identified:

CGA-47197 0-(2-chloro-4-bromophenyl)-n-S-propyl-thiophosphate  
CGA-47196 0-ethyl-0-(2-chloro-4-bromophenyl)-phosphate  
CGA-47195 0-(2-chloro-4-bromophenyl)-phosphate

BCP is stable to acid and basic hydrolysis.

Similar degradation rates and halflives are found for curacron at both 1 and 10 ppm initial concentrations.

The submitted hydrolysis data, when considered jointly, are acceptable.

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#### 4.2 Photolysis in Water and Soil

Under a mercury vapor lamp (radiation  $<290$  nm absorbed and 173 Langleys/hr. or  $2000 \pm 300$  joules/m<sup>2</sup>/sec), curacron degrades in water with a half-life of 27 hours with 62% of the initial material volatilizing in 72 hours. No products were identified but the water pH dropped to 4.6 at 72 hours indicating formation of bromic acids from debromination of the parent (see below).

In 1% acetone, the half-life of parent is 1.8 hours at which time an hexane:aqueous partition gave a 9:1 ratio. The hexane phase was 2 parts parent to 1 part debrominated parent and the aqueous phase contained at least 3 products which were not identified.

During photolysis in methanol, the parent degraded with a half-life of 2 days and with an almost corresponding formation of debrominated parent.

Also, 4-bromo-2-chlorophenol photolyzed in water with a half-life of 1 hour and followed by probably dehalogenation and hydroxylation.

No data on soil photolysis of curacron have been submitted with this or previous submissions. However, judging from the fate in soil, where formation of bound residues is rapid with some release of CO<sub>2</sub>, a study on curacron volatility from soil showing 3% of the fortification (8:1 BCP:parent) volatilizing/hour for the first day, the photolytic fate in water where volatile debrominated parent is formed and the lab fate on cotton leaf surfaces when the parent volatilized, provide sufficient information for the soil photolysis study not to be required for this use.

#### 4.3 Aerobic Soil Metabolism

Over 4 weeks, <sup>14</sup>C ring labeled curacron is degraded in soil under aerobic conditions to primarily (73%) non-extractable material and 17% of the initial activity is released as <sup>14</sup>CO<sub>2</sub>. Only 1.6% remains as parent and 1.8% as 4-bromo-2-chlorophenol. The remainder is unknown polar material (4.3%) and unknown

non-polar material (0.3%). After an additional 8 weeks of aerobic aging, a total of 25.6% of the initial activity has been released as  $^{14}\text{CO}_2$  with a drop in the other chemical fractions analyzed indicating possible microbial degradation of those fractions. An autoclaved soil showed only 1.1% release of initial activity as  $^{14}\text{CO}_2$  over 12 weeks, additionally showing  $^{14}\text{CO}_2$  release to possibly be due to microbial metabolism.

A greenhouse soil degradation study previously reviewed showed no release of  $^{14}\text{CO}_2$  over 12 weeks but identified 4-bromo-2-chlorophenol as the only metabolite (6% at 6 weeks and 3% at 12 weeks).

Other soil data submitted showed 23.8% extractable and 87.7% non-extractable residues at 14 days from a bucket of treated soil planted to lettuce.

There is a clear correlation between the sharp drop in extractable residues and the sharp increase in bound residues. There is also greater degradation of the parent and formation of bound residues with increasing pH. The bound residues formed may be available for uptake by rotational crops and runoff into natural waters.

In soils between pH 5.6 and 7.5 the halflife of the parent is less than 4 weeks. The only degradation product identified is 4-bromo-2-chlorophenol which is never greater than 8% of the initial material applied and drops with increasing time after day 0.

We note that one study reports release of 25%  $^{14}\text{CO}_2$  over 12 weeks of aerobic aging of  $^{14}\text{C}$  curacron in soil while other studies show no release of  $\text{CO}_2$ .

The aerobic soil metabolism studies satisfy our requirement when considered together.

#### 4.4 Anaerobic Soil Metabolism

New data was not submitted.

However, a previously reviewed study showed that after 4 weeks of anaerobic aging preceded by 4 weeks

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of aerobic aging, the non-extractable residues were diminished from 75% to 65% and the  $^{14}\text{CO}_2$  released increased from 17% to 20%. Changes in the polar, unpolar and 4-bromo-2-chlorophenol fractions were slight.

Although only a 4 week anaerobic sample was taken and an anaerobic control was not run, we can conclude that anaerobic soil conditions will not change patterns of degradation of curacron from those under aerobic conditions.

#### 4.5 Effects on Microbes

It is difficult to determine if CGA-15324 and bromochlorophenol significantly inhibit microorganisms involved in biogeochemical transformations occurring in soil and aquatic habitats because of the many discrepancies found between the studies submitted. In a recently submitted study by C. D. Ercegovich (2/15/78), CGA-15324 and bromochlorophenol at 5 ppm significantly inhibited one bacterial population out of nine and six fungal populations out of fourteen tested. Microorganisms were incubated on potato dextrose agar for not more than 13 days or hours (depending on Table 2 or 4, whichever is correct) to determine long term effects.

The results from this study do not agree with a previously reviewed study by Graham and Lawson, 6/7/76 (Bioresearch Labs) where no effects were observed on bacterial, actinomycetes, or fungal populations in soil at rates as high as 250 ppm. Microorganisms were not identified to family name or genera, making it difficult to compare this study with the study done by C. D. Ercegovich (2/15/78).

Microbial studies using a functional approach showed a decrease in nitrification at 50 ppm, while cellulytic activity was enhanced by the addition of 50 ppm CGA-15324. (It should be noted that the cellulose degradation study was unacceptable since cellulose degradation was not followed and microorganisms were not identified.)

#### Effects of Microbes.

Soil metabolism studies using sterile vs. non-sterile soil showed that microorganisms may contribute to the degradation of CGA-15324.

#### 4.6 Leaching Data

A submitted but previously reviewed leaching study (30 cm column) showed insignificant leaching in 3 soils but some leaching in a sandy soil to 20 cm when the equivalent of 8 acre inches was applied to each soil.

The previously reviewed aged leaching study showed minor leaching beyond 6 inches in a sandy soil and insignificant leaching in a silty loam.

This information is acceptable and shows that soils low in organic matter and high in sand permit minor leaching of curacron.

#### 4.7 Field Soil Dissipation

The studies submitted and reviewed showed curacron residues to be not detectable after 15-40 days down to 12 inches in the soil.

We note from the aerobic soil metabolism studies that most of the soil applied curacron becomes bound in 2-4 weeks and would not be detected by the analytical methods used in these field dissipation studies. Therefore, the data are acceptable.

#### 4.8 Rotational Crops

Cotton treated at 1x and 2x (6 and 12 lb. ai/A) the maximum rate for 1 and 2 consecutive seasons with non-labeled curacron and then planted to rotational crops showed no detectable uptake (<0.05 ppm) of curacron residues containing the 4-bromo-2-chlorophenol (BCP) moiety using method AG-283. Recoveries with this method are probably less than 20% of the material taken up by the plant.

$^{14}\text{C}$  residues were found in rotational crops planted 8-10 weeks after treatment with  $^{14}\text{C}$  curacron and harvested at age 14-20 weeks when a total combustion was run. However, when parallel analyses were run on 2 of these plant samples using AG-322, release of 18-20% of the total activity was realized with no detectable (<0.05 ppm) BCP found. Also, basic/acidic refluxing done directly to the plant material released 72% of the total activity with no detectable (<0.05 ppm) BCP found in the organic fraction of an aqueous:organic partition. However, the identity of the organic or aqueous activity is not given. Evidence is strong that the ring moiety is being conjugated to natural plant products. We defer to the Toxicology Branch as to the significance of these residues.

Pending decision from Toxicology Branch that there is no significance, then a rotational crop restriction on curacron use on cotton will not be needed.

#### 4.9 Fish Accumulation

The static exposure system using channel catfish showed bioconcentration factors of 17x for whole body, 8x for edible tissue and 124x for non-edible tissue at day 21 of exposure. However, this previously reviewed study (100-EUP-53, February 1, 1977) was not conducted for the recommended exposure time of 30 days and 14 days for depuration. Also, the amount and identity of residues in water, soil, whole body fish, edible tissue, and viscera were not determined at each sampling interval. This study does not reflect true rates of accumulation and elimination since the fish in this study were infected with parasites and were highly stressed during the experiment.

The flow-through exposure systems using bluegill showed varying results. In one experiment where fish were exposed to 1 ppm  $^{14}\text{C}$ -CGA-15324, muscle tissue exhibited bioconcentration factors of 17x, head portion 24-42x, visceral portion 320-676x and whole fish 60x. Within 24 hours of depuration bluegill had eliminated 90% of radioactivity in the muscle tissues.

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In a second flow-through experiment where bluegill<sub>b</sub> were exposed to a lower amount of CGA-15324 (30 ppm), the fish died after 7-9 days of exposure. These bluegill sunfish exhibited flashing characteristics representative of chemical toxicity. Residues in muscle tissue were not expressed. It should be noted that a lower dose of CGA-15324 produced chemical toxicity and eventual death of the fish in this experiment.

In a third flow-through experiment where bluegills were exposed to 30 ppb CGA-15324, fish began to die again by the ninth day. Bioaccumulation levels reached 1900x in the viscera, 230x in the head and 120x in the body. Parent compound and 4-bromo-2-chlorophenol represented 28% and 14% of the total <sup>14</sup>C-residues in viscera and 62% and 12% in the fish body.

In a fourth flow-through experiment bluegill fingerlings exposed to 1 ppb <sup>14</sup>C-CGA-15324, bioaccumulation factors ranged from 400-500x in the viscera, and 10-40x in head and body. There was insufficient radioactivity to identify metabolites in fish although 33-55% of the total <sup>14</sup>C in water was identified as 4-bromo-2-chlorophenol and 4-bromo-2-chlorophenol sulfate.

In the latter three experiments where fish exhibited chemical toxicity, muscle tissue concentrations of CGA-15324 were not reported. Nevertheless, the data that were reported indicate a potentially serious hazard to nontarget aquatic organisms and contamination of the food web at very low concentrations of CGA-15324.

These five fish studies in combination satisfy the requirement for a fish accumulation study.

#### 4.10 Tank Mix Data

When considered together, the different tank mix studies are acceptable. They show curacron to degrade with a halflife of less than 2 weeks when applied alone or tank mixed with Guthion and to degrade with a halflife of less than a month when applied alone or tank mixed with methyl parathion.

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5.0 Recommendations

- 5.1 The rotational crop data using  $^{14}\text{C}$  labeled curacron, show uptake of  $^{14}\text{C}$  residues, which are primarily conjugated with natural plant products. However, 72% of this  $^{14}\text{C}$  activity is released via basic/acidic refluxing and separates 4:1 in an aqueous:organic partition. But the activity in either fraction is not identified. We defer to the Toxicology Branch as to the significance of these residues.

Pending decision from Toxicology Branch that there is no significance, a rotational crop restriction for curacron use on cotton will not be needed. PM, please coordinate this deferral.

- 5.2 Note to PM: You did not make mention to us of the registrant's request for waivers of the soil photolysis data and the January 20, 1978, Draft Guidelines requirement of adsorption/desorption data. What should be done with these waiver requests?
- 5.3 The data submitted concerning effects on microbes contain too many discrepancies to permit conclusions to be drawn.

In a recently submitted study by C. D. Ercegovich (2/15/78), CGA-15324 and bromochlorophenol at 5 ppm significantly inhibited one bacterial population out of nine and six fungal populations out of fourteen tested. Microorganisms were incubated on potato dextrose agar for not more than 13 days or hours (depending on Table 2 or 4, whichever is correct) to determine long term effects.

The results from this study do not agree with a previously reviewed study by Graham and Lawson, 6/7/76 (Bioresearch Labs) where no effects were observed on bacterial, actinomycetes, or fungal populations in soil at rates as high as 250 ppm. Microorganisms were not identified to family name or genera, making it difficult to compare this study with the study done by C. D. Ercegovich (2/15/78).

Micribial studies using a functional approach showed a decrease in nitrification at 50 ppm, while

cellulolytic activity was enhanced by the addition of 50 ppm CGA-15324. (It should be noted that the cellulose degradation study was unacceptable since cellulose degradation was not followed and microorganisms were not identified.)

- 5.4 The other data requirements in support of curacron use on cotton, including the tank mix use of curacron with methyl parathion or guthion on cotton, have been satisfactorily met.

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