

US EPA ARCHIVE DOCUMENT

EEE BRANCH REVIEWS

DATE: IN \_\_\_\_\_ OUT \_\_\_\_\_ IN 9/27/76 OUT 1/26/77 IN \_\_\_\_\_ OUT \_\_\_\_\_  
FISH & WILDLIFE ENVIRONMENTAL CHEMISTRY EFFICACY

FILE OR REG. NO. 748-161,162

PETITION OR EXP. PERMIT NO. 4F1429

DATE DIV. RECEIVED 9/21/76

DATE OF SUBMISSION 9/21/76

DATE SUBMISSION ACCEPTED 3CID (No)

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

PRODUCT MGR. NO. Taylor (25)

PRODUCT NAME(S) Chloro-IPL 4E; chloro-IPL-10G

COMPANY NAME PPG Industries

SUBMISSION PURPOSE New EC-studies, as requested.

CHEMICAL & FORMULATION Chlorpropham[isopropyl m-chlorocarbamate]

1.0 Introduction

1.1 In response to RD's correspondence relative to the CIPL EC-data gaps noted in our review (8/7/75), PPG's letter (10/7/75) notes:

"The registrant is submitting data to answer...questions asked in RD letter of July 17, 1975 or...protocol which will correct the listed deficiencies."

After reviewing the data and protocol we recommended (11/10/75):

- (a) Sugarbeets replace radishes in the rotational crop study; also, an increase in the number of sampling intervals to show growth dilution.
- (b) Protocols for the other needed studies were either satisfactory or the data submitted in response to RD's request closed the data-gap and made additional study unnecessary.

1.2 PPG's letter (9/21/76) which accompanies the current data emphasizes their concern that the amendments proposed by this application be evaluated on the basis of the old regulation (70-15), the note; "...PPG Industries, Inc., herewith submits three copies of reports...as required by PR Notice 70-15...in response to the specific requests...of July 17, 1975; September 10, 1975 and December 2, 1975... some of the information requested...was presented in our letter of October 7, 1975 (see 1.1)."

1.3 The current EC-data package consists of one volume (As #059292) with the following sub-divisions; there is no table of contents.

- (1) Preface (pg 1); background and pertinent correspondence.
- (2) Summary of Itemized Data Requested (pg 13); Under EC-headings, abstracts of the supporting studies are presented, with the reference and page number of the volume following in parenthesis.
- (3) Bibliography (pg 29); supporting references (44) are listed alphabetically by author.
- (4) Cited References (pg 35); studies are listed which are not in the volume, it's noted; "...they are either readily obtainable or may have been submitted by PPG previously."

1.4

Both the bibliography above (see 3) and the following bibliographies, in which the reference is to microbial soil studies in earlier submissions, contain the following types of data:

(a) Previously Reviewed (8/22/75)

Helling, Charles S. 1971. Pesticide Mobility in Soils I. Parameters of Soil Thin-Layer Chromatography. Proc. Soil Science Soc. of Amer. 35:732-737. Ref #19

Helling, Charles S. 1971a. Pesticide Mobility in Soils II. Applications of Soil Thin-Layer Chromatography. Proc. Soil Science Soc. of Amer. 35:737-743. Ref #20.

Helling, Charles S. 1971b. Pesticide Mobility in Soils III. Influence of Soil Properties. Proc. Soil Science Soc. of Amer. 35:743-748. Ref #21.

Helling, Charles S., Donald D. Kaufman, and Charles T. Dieter. 1971. Algae Bioassay Detection of Pesticide Mobility in Soils. Weed Science 19:685-690. Ref #22.

Bibliography reference Nos. 15, 17, 33, 34, 37, 41, 42, 43, 51, and 53, submitted with Section D, Part 2 of CIPC P.P. No. 1F1119 on December 29, 1970. (pg 19).

(b) Not germane to EC-data requirements

Guzik, F. F. 1976b. Agricultural Chemicals. DV. Synthesis of Isopropyl 3-Hydroxycarbanilate for Toxicity Studies. Internal PPG Industries, Inc. Report BR-20215, dated March 24, 1976. Ref #13.

Nham, Dan. 1976. Acute Toxicity Studies with PPG-194, isopropyl-3-hydroxycarbanilate (436-1213). BIO-TEST report to PPG Industries, Inc., IBT No. 8530-08641, dated July 8, 1976. Ref #28.

Pensyl, J. 1974. An Improved Gas Chromatographic Method for the Determination of PPG-124 in Alfalfa. Internal PPG Industries, Inc. Report BR-17000A, dated June 7, 1974. Ref #29.

Reinert, Howard K. and Geoffrey St. E. Parke. 1975. Report on Static 96-Hour Toxicity Study of PPG Industries, Inc. Sample of CIPC chemical in rainbow trout and rainbow trout. Cannon Laboratories, Inc. Report, Laboratory Number 5E-8034, dated September 17, 1975. Ref #30.

Strang, R. H. Agricultural Chemicals. CCLXXII. Report on the Growing, Sampling and Shipping of Turnips and Orchardgrass Grown in the <sup>14</sup>C-CIPC Treated Soil at Boyce Thompson for CIPC Metabolite Study. Internal PPG Industries, Inc. Report BAR-18528, dated April 19, 1973. Reg #32.

Wiedmann, J. L. and D. M. Mattle. 1976. CIPC and PPG-124 Residues in Yuchi Arrowleaf Clover, 1976 Crop. Internal PPG Industries, Inc. Report BTS-20352, dated July 20, 1976. Ref #37.

Wiedmann, J. L. and J. Pensyl. 1975. CIPC and PPG-124 Residues in Water-Run Alfalfa from California and Arizona. Internal PPG Industries, Inc. Report BTS-19773, dated May 29, 1975. Ref #38.

Wiedmann, J. L., W. H. Trent, and D. M. Mattle. 1975. CIPC and PPG-124 Residues in Onions, 1973-1975 Crops. Internal PPG Industries, Inc. Report BTS-19991, dated October 17, 1975. Ref #39.

Wiedmann, J. L., J. Pensyl and D. M. Mattle. 1975. Comparison of CIPC and PPG-124 Residues in Soil, Water, and Alfalfa from Water-Run-Treated Alfalfa Fields. Internal PPG Industries, Inc. Report BTS-19789, dated June 6, 1975. Ref #40.

(c) Ancillary References

Bartha, Richard and David Pramer. 1965. Features of a Flask and Method for Measuring the Persistence and Biological Effects of Pesticides in Soil. Soil Science 100:68-70. Ref #1.

Bonner, W. P. 1975. Report of Test Number 00OMP1-318-2A, conducted by United States Testing Company, Inc., Memphis, Tennessee, dated November 14, 1975. Ref #2.

Bonner, W. P. 1975a. Report of Test Number 00OMP1-318-3A, conducted by United States Testing Company, Inc., Memphis, Tennessee, dated November 14, 1975. Ref #3.

Disco series. 1975. Description of the Disco Series of soils from the National Cooperative Soil Survey, U.S.A., Established series Rev. GOW-ECAR, March 2, 1975. Ref #4.

Hannah, L. H. 1975. Personal correspondence to Dr. Warren Zick, PPG Industries, Inc., dated September 23, 1975, transmitting copy of Method D-4, dated June 20, 1967 (AD-76), LASO PARENT, PART II - CHEMICAL ANALYTICAL RESIDUE METHODS. Ref #17.

Hanovia Photochemical Equipment for Laboratory-Scale Reactions (EH-411), Hanovia Lamp Division, 100 Chestnut Street, Newark, New Jersey. Ref #18.

Kaufman, D. D., J. R. Plimmer, and U. I. Klingebiel. 1973. Microbial Oxidation of 4-Chloroaniline. J. Agr. Food Chem. 21:127-132. Ref #23.

Kearney, Philip G. and Arnold Kontson. 1976. A Simple System to Simultaneously Measure Volatilization and Metabolism of Pesticides from Soils. J. Agr. Food Chem. 24:424-426. Ref #24.

Lavanish, J. M. 1975. PPG Industries, Inc., Inter-office Correspondence to Warren Zick, Subject: Photodegradation of CIPC, dated August 1, 1975. Ref #25.

Muscatine series. 1969. Description of the Muscatine series of soils from the National Cooperative Soil Survey, U.S.A., Established series Rev. RID-TEF: January 8, 1969. Ref #27.

Rutledge, E. M. 1975. Letter to W. H. Zick, dated November 17, 1975, enclosing a description of the Keo soil series as taken from the Pulaski (Arkansas) County Soil Survey Report. Ref #31.

Trent, W. H. 1976. Dynamic Oxygen Tube Combustion of Plant Tissues and Soils Containing  $^{14}\text{C}$ -Ring Labeled CIPC for Liquid Scintillation Counting. Internal PPG Industries, Inc. Report BR-20297, dated June 9, 1976. Ref #33.

Wiedmann, J. L. 1975. Summary of Research Reports Issued by the Barbarton Technical Center Involving  $^{14}\text{C}$  Labeled CIPC and PPG-124. Internal PPG Industries, Inc. Memo J. L. Wiedmann to W. Zick, dated August 8, 1975. Ref #34.

Zapp, Richard. 1975. Abstract in Quarterly Summary - (April 1976) of Southeastern Environmental Research Laboratory, Athens, Georgia. Ref #42.

Blake, J. and D. D. Kaufman. 1975. Characterization of acylanilidehydrolyzing enzyme(s) from Fusarium oxysporum Schlecht. Pesticide Biochem. Physiol. 5:305-313. Ref #43.

Fletcher, C. L. and D. D. Kaufman. 1975. Hydroxylation of monochloroaniline pesticide residues. Abstract No. 199, Weed Science Soc. Amer. Meeting. Draft of full text via personal correspondence D. D. Kaufman to W. H. Zick. Ref #44.

Bibliography reference Nos. 5, 12, and 28, submitted with Section D, Part 1 of CIPC P.P. No. 4F1429 on August 22, 1973. (pg 19); As #(92175(1-4-72)).

(d) Ancillary data (microbial in soil) not with package

Bibliography reference Nos. 27 and 29, submitted with the Substantive Amendment of CIPC P.P. No. 2F1276 on February 9, 1973.

(e) Data needed for the purpose use (also, see 3.0)

Ecke, G. G. 1976. Agricultural Chemicals. DXXVII. Qualitative Investigation of CIPC Metabolites in Catfish. Internal PPG Industries, Inc. Report BR-20348, dated June 11, 1976. Ref #5.

Includes:

Smith, Dathleen S. and David L. Merricks. 1976. Report on Catfish Tissue Residue Levels Following Exposure to <sup>14</sup>C-CIPC. Cannon Laboratories, Inc. Report 5E-8033, dated January 30, 1976. Ref 5a.

Ecke, G. G. 1976a. Agricultural Chemicals. DXXXII. Qualitative Investigation of CIPC Metabolites in Bluegill Sunfish: Preliminary Report. Internal PPG Industries, Inc. Report BR-20316, dated June 21, 1976. Ref #6.

Ecke, G. G. 1976b. Agricultural Chemicals. DXXXIX. Qualitative Investigation of CIPC Metabolites in Bluegill Sunfish: Final Report. Internal PPG Industries, Inc. Report BR-20315A, dated July 15, 1976. Ref #7.

Includes:

- Smith, Kathleen S. and David L. Merricks. 1976a. Report on Bluegill Sunfish Tissue Residue Levels Following Exposure to <sup>14</sup>C-CIPC. Cannon Laboratories, Inc. Report, Laboratory Number 6E-1100A, dated June 25, 1976. Ref #7a.
- Ecke, G. G. 1976c. Agricultural Chemicals. DXLVI. Rotational Crop Study - Extraction of Sugar Beet Roots. Internal PPG Industries, Inc. Report BR-20401, dated August 16, 1976. Ref #8.
- Ferguson, C. E. 1976. Characterization of Soil Bound Residues from the Aerobic/Anaerobic Soil Metabolism of <sup>14</sup>C-Ring Labeled CIPC. Part III. Internal PPG Industries, Inc. Report BR-20350, dated July 19, 1976. Ref #9.
- Guzik, F. F. 1975. Agricultural Chemicals. CDLXXVII. Preliminary Investigation of the Photolysis of CIPC and IPC in Water. Internal PPG Industries, Inc. Report BR-20042, dated November 11, 1975. Ref #10.
- Guzik, F. F. 1976. Agricultural Chemicals. CDXCI. Photolysis of Carbon 14 Ring-Labeled Chlorpropham (CIPC) in Water. Internal PPG Industries, Inc. Report BR-20148, dated February 2, 1976. Ref #11.
- Guzik, F. F. 1976a. Agricultural Chemicals. DIII. Identification of Yellow Photoproduct Obtained from Photolysis of CIPC in Water with Acetone as Sensitizer. Internal PPG Industries, Inc. Report BR-20180, dated February 24, 1976. Ref #12.
- Guzik, F. F. 1976c. Agricultural Chemicals. DIX. Aerobic/Anaerobic Soil Metabolism of CIPC. Part I. Internal PPG Industries, Inc. Report BR-20252, dated April 28, 1976. Ref #14.
- Guzik, F. F. 1976d. Agricultural Chemicals. DXXXIV. Characterization of C-14 Activity in Aqueous Fraction from C-14 CIPC Photolysis Solution. Internal PPG Industries, Inc. Report BR-20328, dated June 29, 1976. Ref #15.

Guzik, F. F. 1976e. Agricultural Chemicals. DXLIV. Analysis of Water from Cannon Laboratories' Static Catfish Study. Internal PPG Industries, Inc. Report BR-20377, dated August 6, 1976. Ref #16.

Maliani, Nancy. 1976. CIPC and CIPC + PPG-124 Interaction Study (Exhibit E), for PPG Industries, Inc. by Morse Laboratories, Inc., Sacramento, California, Laboratory No. 97021, dated September 10, 1976. Ref #26.

Wiedmann, J. L. 1976. Characterization of Soluble <sup>14</sup>C Species from the Aerobic/Anaerobic Soil Metabolism of <sup>14</sup>C-Ring Labeled CIPC. Part II. Internal PPG Industries, Inc. Report BR-20316, dated June 24, 1976. Ref #35.

Wiedmann, J. L. 1976a. CIPC Photolysis Products - Molecular Weight Estimation. Internal PPG Industries, Inc. Report BR-20364, dated August 10, 1976. Ref #36.

Wiedmann, Jerome, D. Kish, W. H. Trent, and W. H. Zick. 1976. Characterization and Quantitative Analysis of CIPC Residues in Three Rotational Crops, Wheat, Lettuce and Sugar Beets. Internal PPG Industries, Inc. Report BR-20402, dated September 7, 1976. Ref #41.

2.0 Directions for Use :

2.1 Soybean applications\* (Petition 4F-1429)

(A) Proposed labeling\* (748-161) first received 8/28/74.

- (1) "SOYBEANS - Pre-emergence following pre-plant incorporated treatment of trifluralin at the recommended rate of 1 to 2 pints (1/2 to 1 lb. trifluralin) per acre. At planting or immediately after apply Furloc Chloro IPC EC at 2 to 3 quarts (2 to 3 lbs CIPC) per acre in sandy loam and medium soils (loam, silt loam and silt) and the higher rate for heavy soils (clay, clay loam and silt clay)..."
- (2) "SOYBEANS - Pre-emergence - Apply 4 to 8 quarts in 20 - 40 gallons of water per acre immediately after planting or prior to emergence. For early planting or on sandy loam soil apply 4 quarts per acre, for summer plantings or on clay loam soils apply 6 quarts per acre, and for late plantings on heavy soil apply 8 quarts per acre."

(3) "Soybeans - FURLOE CHLORO IPC EC PLUS LASSO TANK MIXTURE.

Broadcast (overall treatment) - Apply the tank mixture in sufficient water (5 to 40 gal./A) to provide uniform distribution on the soil surface after planting and before emergence of beans... See the following table for recommended rates of Furloe, Chloro, IPC EC plus Lasso EC on various soil types:"

	Broadcast Rate (Quarts/A or pounds active ingredient/A)		
	Furloe Chloro IPC 4EC		Lasso 4EC
	Less than 5% Organic Matter	More than 5% Organic Matter	All Levels of Organic Matter
Sand & Sandy Loam	2	2	+ 2
Loam, Silt Loam, Silt	2 to 3	2.5 to 3	+ 2 to 2.5
Clay, Clay Loam, Silt Clay	2 to 3	3	+ 2.5 to 3

(B) Additional changes proposed with this submission.

(1) "Soybeans - preplant incorporated - TANK MIX Furloe Chloro-IPC EC plus Treflan EC..."

To control broadleaf weeds, uniformly apply the tank mixture at the following rates per acre, broadcast in 10 to 40 gallons of water:

Soil Type	Pints Treflan	Quarts Furloe IPC
Light (Sandy & Sandy Loam)	1 (1/2 lb.)	2 (2 lbs.)
Medium (Loams)	1-1/2 (3/4 lb.)	2-1/2 (2-1/2 lbs.)
Heavy (Clay, Silt, & soils over 5% Organic Matter)	2 (1 lb.)	3 (3 lbs.)

Incorporation of the tank mixture - (See Treflan label for full instructions) Incorporate the chemicals thoroughly into the soil within four hours of application..."

- (2) "Soybeans - preplant incorporated - Tank Mix Furloe Chloro-IPL EC plus Vernam 6-E"

Preplant soil incorporation or post plant soil incorporation of tank mixture...will give control of broadleaf weeds. On soybeans in the northcentral area of the U.S. apply the following rates per acre broadcast in 10 to 50 gallons of water:

<u>Soil Type</u>	<u>Pints of Vernam</u>	<u>Quarts Furloe CIPC</u>
Light (Sandy)	2-2/3 (2 lbs.)	2 (2 lbs.)
Medium to Heavy (Sandy Loam to Clay Loam)	3-1/3 (2-1/2 lbs.)	2-1/2 (2-1/2 lbs.)
Heavy (Clay)	4 (3 lbs.)	3 (3 lbs.)

Incorporation - (See the Vernam label for full instructions) The chemicals must be incorporated into the soil immediately (within minutes) after application. For preplant...and for post plant...incorporation, use power-driven cultivation equipment..."

2.2 Environmental precautions

"Do not apply where run-off is likely to occur. Do not apply when weather conditions favor drift. Do not contaminate water by cleaning of equipment or disposal of wastes. Do not re-use container, destroy by crushing or perforating and burying in a safe place"

3.0 Discussion of data

3.1 Photodegradation of CIPC

(A) (H) "Photodegradation of carbon 14 ring-labeled chlorpropham (CIPC) in Water"; Guzik, F. F. [Ref #11 (pg 135); Report BR 20118 (2/2/76) as no. 005292 (2/2/76)]

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An aqueous solution of ring-labeled(14C) CIPC(4.0 ppm) was irradiated (104 hr) in A Quartz Hanovia #654(1-qt) photoreactor. The 200-watt mercury-vapor lamp with filter (2800 Å) approximated normal insolation. The solution which was prepared with water distilled over potassium permanganate was maintained at 25°; the solution was stirred; dark controls were included in the study.

The analysis of periodic samples included not only 14C assays(LSC) and chromatographs (HPLC) of the solution but also 14C-assays(LSC) and chromatographs (TLC/ autoradiographs) of concentrated methylene chloride extracts of the solution.

Summary; Percentage figures(cal) from Tables I and II

<u>Exposure(hrs)</u>	<u>Soln. Analysis(1)</u>			
	<u>CIPC</u>	<u>3-HO-IPC(4)</u>	<u>(2)</u>	<u>(3)</u>
0	100	0	0	0
8	96.9	4.4	-	2.9
24	86.3	10.9	2.8	4.6
32	83.9	12.7	3.4	-
48	75.8	21.1	3.1	9.9
56	80.4	27.7	-	6.2
72	67.5	30.3	2.2	7.7
80	66.3	29.4	4.3	11.1
96	58.2	32.7	9.1	10.7
104	55.1	38.5	6.4	11.1
(130)*	(50.0)	(37.5)	(12.5)	-

Note

(1) The activity of the initial solution (4.0 ppm) and the dark controls was approximately 3600 dpm/ml.

(2) Degradates in this column are characterized as water soluble (polar) materials with a molecular weight greater than 700 (ca 10.5%) and less than 700 (ca 2.0%) they were not extractable with methylene chloride or other solvents (Ref 36, pg. 399).

The activity remaining in the aqueous phase following methylene chloride extraction includes small amounts of both CIPL and 3-HO-IPL. Column(2) figures are taken as the difference between CIPL plus 3-HO-IPL, and 100%.

- (3) Activity (%) in the aqueous phase following extraction.
- (4) *Isopropyl 3-hydroxycarbanilate is the principal photolysis product.*
- (4)\* The CIPL-half-life figure of 130-hrs is extrapolated from a log-plot of CIPL concentration versus time. Other runs at slightly different conditions indicated the CIPL-half-life at 140 hrs (6.5 ppm) and 80 hrs. (plain distilled water).

Conclusion: (A)

- (a) Photodegradation studies are not complete; both the current and previous requirements include data on soil. Further, if its determined that re-entry data is needed vapor-phase photolysis will also be required.
- (b) Ref #11 together with the photolysis studies below (sec. 2 and 3)\*\* provides adequate data on aqueous photolysis. CIPL half-life varied in distilled water from 80-140 hrs. The half-life is probably somewhat less in the environment, since CIPL is subject to photosensitization. The principal photoproducts are identified.

Starts  
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(e) (2) "Preliminary Investigation of the Photolysis of CIPL and IPL in Water"; Guzik, F.F. [ref #10 (pg 129); Report BR 20042 (11/11/75); As "095292(9/21/76)].

The study was made with unlabeled CIPL. Quantities of both aqueous and acetone solutions of the ai ( 52 ppm) were irradiated in quartz, a Rayonet photochemical reactor was used. Samples were periodical withdrawn and analyzed; methylene chloride extracts were concentrated and chromatographed (TLC/auto-radiograph)

\*\* Note Ref #16; "Analysis of Water from cannon Laboratories' static catfish study". The work was undertaken in an attempt to identify a degradate which would account for the exceptionally high mortality rate. ~~Since very little of the main mortality rate.~~ Since very little of the main photoproduct was found the toxic agent was assumed to be a soil metabolite.

<u>Solution</u>	<u>Photoproducts</u>	<u>Half-life</u>
(1) Water	3-HO-IPL	15 minutes
(2) 2% acetone	3-10-IPL yellow ppt.*	5 minutes

\*2-isopropoxycarbonylamino-1,4-benzoquinone (Ref. #12 pg. 146)

Conclusions <sup>B</sup>(2):

The study supplements reference #11 (see (1)). Small amounts of the yellow precipitate may occur in the environment as the result of photosensitization.

(c) (d) "Characterization of C-14 Activity in Aqueous Fraction from C-14 CIPC Photolysis solution"; Guzik, F.F. [Ref #15 (pg 165); Report 20328(6/29/76); As #095292 (9/21/76)]

Testing details as above [(sec (2))]; however in this study CIPC was ring-labelled (14C) and the solution concentration was lower (4.0 ppm).

Results:

The photoproducts accounting for the activity (1.2-1.5%) remaining in the aqueous phase (1.2-15% total activity) were identified as:

- (a) Small amounts of 3-HO-IPL (ca 0.5 ppm) and CIPC (0.1 ppm) by TLC/LSC.
- (b) And as polar compounds with a molecular weight of more than 700 (85%) and less than 700 (15%) [ref #36; pg 399].

Conclusion <sup>C</sup>(3):

The study provides additional characterization = data on the photolysis products.

### 3.2

#### Comparative Aerobic/Anaerobic Soil Metabolism Studies

(a) Part I: "Agricultural Chemicals. DIX Aerobic/Anaerobic Soil Metabolism of CIPC"; Guzik, F.F. [Ref #14 (pg 154); Report BR 20252 (4/28/76); As 095292 (9/21/76)]

Experimental:

The samples were incubated at 23°C ( $\pm$  4°) under subdued lighting in a hood. Each of eight biometer flasks contained 60-grams of wet (50 gm. dry) ~~moisture soil (sand 21.3%, silt 64.3%, clay 11.3, O.M., 0.7%)~~ spiked at 5.00 ppm with 14C-ring-labeled CIPC. Incubation was limited to either 9-week or 13-week periods.

Aerobic Systems: After 2-weeks half of the eight flasks were flooded with water (100 ml), placed under nitrogen, and the incubation continued anaerobically.

Summary of data:  
Evolved Carbon-dioxide (LSC-dpm's)

Time (wks)	Aerobic Flasks				1	Anaerobic Flasks**			
	1	2	3	4		2	3	4	
Pre-test	835	676	655	756	716	669	806	772	
Pre-test	1450	1882	2134	1675	1794	1876	1477	1553	
1	988	1808	2367	1417	225	192	196	108	
2	1365	2115	2743	1501	174	86	125	83	
3	1080	1423	1864	1548	30	14	44	27	
4	1043	1654	1724	1319	28	14	28	52	
5	1383	1601	2744	1474	55	29	42	0	
6	1243	1379	1834	1099	44	0	43	31	
7	1039	872	1134	885	15	30	44	15	
8	837	1064	2302	918	72	14	42	44	
9	868	867	1213	992	0	14	30	15	
10	-	-	1597	736	-	-	69	29	
11	-	-	1329	928	-	-	178	85	
12	-	-	1164	700	-	-	216	138	
13	-	-	1164	700	-	-	216	138	
Total *	12167	15341	25968	16648	3153	3038	3556	3090	
Equiv %	5.1	7.6	1.3	8.3	1.6	1.5	1.8	1.5	

\* The initial activity in each flask was about  $2.10^5$  dpm (pg 156)

\*\* Most of the reported carbon dioxide from the anaerobic flask evolved during the aerobic pre-test period.

**Conclusions (Part I):**

- (a) Aerobic rather than anaerobic metabolism is shown to be the principal degradation process in Wooster silt loam.
- (b) Although the company's protocol for this study, which we reviewed proposed sampling periods of 60 and 90 days; the present and past Guideline Requirements are for data through a 90% decline or for

one year. Since the sampling was at 63 and 91-days the study was sufficiently long only by the proposed protocol. (see Part II)

(B) Part II: "Characterization of the Soluble <sup>14</sup>C species---"; Wiedmann, J.L. [Ref 35(pg 384); Report BR-20316(6/24/76); As 095292(9/21/76)]

Experimental (flow chart, pg 390):

Soil and water from the biometer flasks (Part I(a)) and extractives from the P.V.-foam plug were studied.

Water: the aqueous phase (anaerobic only) was extracted with hexane and the extract chromatographed by TLC (LSC/autoradiograph) and GLC[see 3.1.1 analysis (B)].

Soil; both the aerobic and anaerobic (dried) samples were extracted (24 hrs) with hexane. The extracts were assayed (<sup>14</sup>C) and chromatographed by TLC/autiograph) and GLC [see 3.1.1 analysis (B)]. The hexane extracted soil was then extracted with water. Aliquots of the water extract were assayed (LSC) and subjected to enzymatic hydrolysis [glucuronidas (30 mg); pronase 20 mg; cellulase (50 mg); in 15 gm of water, buffered at pH5]. The hydrolysis (R. temp) was discontinued after 3-days.

Summary:

%<sup>14</sup>C-Distribution (Avg's); Excerpts from Tables III thru <sup>IV</sup> II

Fraction (table)	Aerobic		Anaerobic	
	9-wk	13-wk	9-wk	13-wk
<sup>14</sup> C-CO <sub>2</sub> (II)	8.3	12.9	1.9	2.0
0-2 wks	1.5	1.6	1.6	1.4
3-11 wks	6.8	8.8	0.4	0.3
12-15 wks	-	2.6	-	0.3
P.U.-plugs				
CIPC(pg387)	0.8	1.2	1.5	1.6
In water (III)	-	-	3.4	3.7
CIPC(III)	-	-	2.0	3.1
Not identified	-	-	2.0	3.1
Extracts*				
hexane (IV)	23	17	31	26
Aqueous (V)	0.6	1.0	1.4	2.4
Extr. soil(X)**	44	61	37	44
Totals	75%	93%	96%	80%

\*The extracted activity was identified as follows:

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- (a) Hexane; assays (TLC/LSC) indicate only CIPL [table V]
- (b) Aqueous; most of the activity steam-distilled and was assumed to be unextracted CIPC; "---hexane was a poor choice as participating solvent---future efforts will probably involve use of chloroform or methylene chloride---" (pg 387).

\*\* See Part III(c)

In this part of the study the activity of the spiked samples (5.0 ppm) averaged  $1.64 \cdot 10^5$  dpm.

#### Summary and conclusion (Part II)

- (a) The material balances average 84% (aerobic) and 88% (anaerobic).
  - (b) Extensive soil binding is indicated:
    - (i) both studies show a 17% increase between the 9th and 13th weeks (ca 4.25%/wk)
    - (ii) However, based on total binding at 13 weeks of 61% (aerobic) and 44% (anaerobic), the binding rates may differ.
  - (c) A estimate of the CIPC degradation rate based on  $^{14}\text{C}$ - $\text{CO}_2$  evolution depends on both the CIPC binding rate and degradation rates of the bound and unbound CIPL. For the purpose of a rough approximation it is assumed that the degradation rate of the bound CIPC is much less than the unbound. The degradation is then (at 10 weeks) ca 2.2% per week [4.5% / 4 weeks / 50%] aerobically. The overall loss rate ca 6.5% week (10th week) being the sum of the binding and degradation rates.
  - (d) The study is not acceptable by either the past or current guidelines; both required data through a 90% decline or one year, for the proposed use. Data through two half-lives or six months is now required for disposal assessment.
  - (e) Degradation products which would account for the evolved carbon dioxide ( $^{14}\text{C}$ ) were presumable soil bound.
- (C) Part III: "Characterization of Soil Bound Residues from the Aerobic/Anaerobic Soil Metabolism of  $^{14}\text{C}$  Ring Labelled CIPC"; Ferguson, C.E. [Ref. 9 (pg 114); Report BR 20350 (7/19/76); As No 095292(9/21/76)]

#### Experimental (Flow chart pg. 119):

After hexane and aqueous extraction (see Part II) the soils were further extracted with 0.5N NaOH. The insolubles were assayed by combustion ( $^{14}\text{C}$ ); the alkaline extract was then acidified

(pH1) to separate humins (soluble) from fluvic acid (insoluble). Both phases were assayed by <sup>14</sup>C(25C).

Summary:  
% <sup>14</sup>C Distribution (Avg's); Excerpts from Table III

Fraction	Aerobic		Anaerobic	
	9 wk	13 wk	9-wk	13-wk
Caustic Extrs:				
Humins	5	6	2	4
fulvic A.	20	25	15	17
Insol.	16	20	16	17
Total, %	41	51	33	38

Conclusion (Part III)

- (a) Somewhat more than half of the bound residues were extracted with alkali (0.5N); or 15 to 20% of the applied remained bound.
- (b) Most of the alkaline extracted activity was associated with the fluvic fraction; the activity was distributed in a ratio of about 4 to 1.

3.3

Rotational crop studies

"Characterization and Quantitative Analysis of CIPC Residues in Three Rotational Crops, Wheat, Lettuce and Sugarbeets"; Wiedmann, J.L.; Kish, D.; Trent, W.H.; Zick, W.H. REF #81 (pg 490); Report BR 20402 (4/7/76); As No. 095292 (9/21/76)]

Except for some uncertainty in the length of the length of the aerobic-aging period, the study follows the reviewed protocol.

Flats (8" X 10" X 8");

(a) Cold (3); these were filled (6") with pesticide free Wooster silt loam (sand, 24.3%; silt, 64.4%; clay, 11.3%; O.M., 0.7%).

(b) Hot (3); these contained the same Wooster silt loam (4") under aged spiking soil (2"). The spiking soil was prepared by treating (2 lbs A/A) the Wooster silt loam with ring <sup>14</sup>C-labelled CIPC. After spiking (1/3/73) the soil was stored (0°C) until aerobic aging was initiated. The aging consisted in planting the soil to some one of the following crops: turnips (1/11/73); soybeans (3/6/73); orchardgrass (3/29/73). The harvest dates were: turnips

(4/4/73); soybeans (3/6/73); orchardgrass (3/29/73). The soil was then stored frozen until used (3/1/76) as the spiking soil in this study. A 90-day aging period was intended. However, the report notes; "...it cannot be definitely established from which of the flats(crops) this soil was taken...the exact aging time for the soil is not known but it would be on less than 65 days and not more than 92 days."

**Growing conditions:**

The work was done in a hood using plastic lined flats (6) provided with drain holes. Lighting (15 on/9off) was artificial; watering was both subterraneous and topical, as needed; humidity 60% at 80° F. Each crop was grown in both a cold-flat and a hot-flat.

**Sampling:**

Both shoots and roots from all plants, and soil samples from the flats were collected during the growth period.

**Analysis:**

(a) <sup>14</sup>C-assay: a Packard scintillation counting instrument (2425) was used in the following procedures:

- (i) freeze-dried plant samples were combusted and the <sup>14</sup>C -CO<sub>2</sub> trapped and counted.
  - (ii) other samples were subjected to a steam distillation, after a preliminary alkaline hydrolysis to free 3-chloro-aniline from CIPL-residues, the distillate was extracted (toluene) and an aliquot was assayed (LSC).
- (b) GLC/EC; a second toluene aliquot (see above, b) was cleaned-up (silica-gel) and chromatographed.

**Characterization (REF #8, pg 107):**

- (a) Protocol for this part of the study was not submitted for review.
- (b) The data is limited to the CIPL residues in sugarbeet root.
  - (i) the samples were first extracted with methanol then both the insolubles and methanol solubles, after volatilizing methanol, were extracted with methylene chloride, partitioned with 1% NaCl, back-washed, and the separated fractions combined with those of step (ii).
  - (ii) Step (i) insolubles, after an acid (6N-HCl) extraction, were combusted to <sup>14</sup>C-CO<sub>2</sub> (LSC). The acid solution, after methylene chloride extraction, was assayed (LSC). Methylene chloride solubles were chromatographed (see iii).

(iii) Step (1) aqueous solubles, after methylene chloride extraction, were subjected to hydrolysis (enzymatic) followed by pentane extraction. Activity remaining in the aqueous phase was assayed (LSC). Pentane and methylene chloride extractables, also those of step (11), were transferred to benzene after volatilization of the solvents. The combined extracts were chromatographed and the separated fractions assayed (LSC).

Data Summary  
 Rotational Crop Residues (ppm). [Table II pg. 501]

Crops	Aft. Seeding (days)	Controls			Test Plants		
		"14C"(1)	GLC-EL(2)	"14C"(3)	"14C"(1)	GLC-EL(2)	14C(3)
Lettuce	14	0.02	2.8	<0.01	0.31	0.48	0.04
Lettuce	37	0.02	0.6	<0.01	0.19	0.16	<0.02
Lettuce	63(3)	0.01	-	-	0.04	0.16	<0.01
Wheat(plant)	10	0.01*	-	-	0.10	-	-
Wheat(plant)	37	0.02	0.11	<0.01	0.08	1.48	0.06
W. stem	56(3)	0.03	-	-	0.21	0.57	<0.01
S. beets	10	0.01*	-	-	0.19	-	-
S.B-tops	10	0.01	0.04	< 0.01	0.06	0.14	<0.01
SB-Roots	37	0.02	-	-	0.70	*	*
SB-tops	63(3)	0.01	-	-	0.07	0.30	0.01
SB=roots	63	0.01	0.08	0.01	0.27	0.12	0.01
Averages(ppm)		0.016	0.20	<0.01	0.18	0.41	0.02

Notes:

- 1 Total "14C" assays.
2. Total CIPL-Residues based on steam distilled chloro-aniline after clean-up.
3. "14C"-assays of steam distilled chloro-aniline before clean-up.
4. Days from seeding to harvest

\*see conclusions (b)

Conclusion

(a) Definite CIPL-residues are reported in sugarbeets and marginally significant residues are indicated in lettuce and wheat. Therefore studies with the formulated product will be required to determine when residues will not occur in sequential crops under actual use conditions; these studies would be required under both the old and new guidelines.

The applicant explains the CIPL-residues resulted from an unfortunate contamination of the growing area with cold CIPL; an excessive dis-

-prepancy is noted between the GLC averages (0.41 ppm) and the averages by 14C assay (0.02 ppm). If the residues occurred as the result of contamination the work should be repeated or the studies under actual use conditions will be needed. The data could be explained on the basis of bound CIPL residues in the potting soil.

- (b) Characterization of the sugarbeet residue (0.70 ppm)  
(i) about 1.8% of the activity (0.013 ppm) is tentatively identified as CIPL and its three principal metabolites.  
{isopropyl 5-chloro-2-hydroxycarbanilate;  
isopropyl 3-chloro-4-hydroxycarbanilate;  
1-hydroxy-2-propyl 3-chlorocarbanilate}

(ii) the remaining extractable activity was characterized only on the following basis:

- Water solubility following methylene chloride extractions (24%)
- Activity not extracted (74%).

3.4

"CIPL and CIPE plus PPG-124 Interaction Study" Mallani, N; Dewey, M.L. [Ref #26 (pg. 223); Report 97021 by Morse Laboratories, Inc. (9/10/76). As 095292]

The studies which are "cold" follow without significant differences the reviewed protocol. [exhibit E; pg 314; As #094837 10/10/75)].

Characteristics of the test soils.

Sandy loam: sandy 76.8%; silt 16.0%; clay 7.2%; O.M. 1.7%, pH 5.8; CEC 12.3 Meq/100gm

Silt loam: sand 22.4%; silt 60.4%; clay 17.2%; pH 6.3; C.E.C 21.8  
MEQ MEW/100 gm.

After adjusting moisture to 18% the soils were incubated aerobically (R. Temp) for two weeks. Soil Trays (16 cm x 30 cm x 9 cm) were then prepared with each soil and the degradation of CIPL and the interaction herbicides were determined through, at least the second half-life (10-200 days), after the following series of spikings:

- (a) A series with CIPL (5.00 ppm) alone and each of the interaction herbicides. (5.00 ppm).
- (b) With CIPL (5.00 ppm) plus PPG-124 (1.25 ppm) and each of the interaction herbicides (5.00 ppm) alone, also CIPL (5.00 ppm) alone.

(c) Each of the interaction herbicides (5.00 ppm) alone also CIPL (5.00 ppm) alone.

The testing included recovery data and soil blanks for each herbicide. Soil samples were collected, extracted with hexane, and the extracted herbicides assayed by GLC using a Varian instrument (#2100) equipped with a conductivity detector. Only CIPL and PPG-124 were determined on the same column; details for the assays are given (exhibits L thru Q). The methodology appears adequate; the average recovery figures were: 81% CIPL; 65% PPG-124; 79% Treflan; 88% Tolban; 74% Vernam; 87% Lasso.

Summary of data:

Estimates\* of the first (2.5 ppm) and 2nd (1.25 ppm) half-life's of CIPL and the interaction herbicides from data-graphs\*\* (starting pg. 274 in the data volume)

Spiking Herbicide(s)	CIPL-half life(days)				Interaction herbicides; half life(days)			
	Sandy Loam		Silt Loam		Sandy Loam		Silt Loam	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd
CIPL**	17	38	12	34	-	-	-	-
Treflan	-	-	-	-	56	119	28	115
Tolban	-	-	-	-	56	96	61	116
Lasso	-	-	-	-	6	14	6	13
Vernam	-	-	-	-	2	10	4	7
CIPL, Treflan	14	38	18	38	61	135	29	143
CIPL, Tolban	24	67	24	82	80	133	105	138
CIPL, Lasso	19	27	23	(33)	7	18	5	12
CIPL, Vernam	(26)	-	25	(56)	4	12	6	10
Both CIPL, PPG-124**	55	82	30	74	-	-	-	-
with Treflan	48	79	37	68	74	150	58	143
with Tolban	54	88	28	60	125	(210)	106	140
with Lasso	(68)	-	(71)	-	11	20	6	14
with Vernam	(71)	-	(67)	-	8	13	11	13

\*The tests were started with CIPL and the interaction herbicides at 5.00 ppm.

\*\*Graphs were prepared from the average of two corrected GLC assays; however, both the CIPL and "CIPL/PPG-124" figures are averaged from four graphs.

NOTE: The parenthesis include extrapolated figures.

Data comments:

Soil persistence, as indicated by the first half-life, was increased:

- (1) CIPL from 2-weeks to 3-5 weeks by Tolban<sup>Tolban</sup> alone; to 8-4 week by PPG-124 alone. The effects were not additive. CIPL persistence was increased most in the sand loam (Disco) soil.
- (2) Among the interaction herbicides the following increases are noted:
- (a) Treflan from 8-4 weeks to 10-12 weeks by the CIPL/PPG-124 combination.
  - (b) Tolban from 8-9 week to 11.5-15 week by CIPL alone; to 18-15 weeks by the CIPL/PPG-124 combination.

**Conclusions:**

The data shows herbicides of the proposed tank-mixes will reach their first half-life within 18-weeks and before a subsequent herbicide application would be required. (~~Field studies will not be needed~~)?

3.5

**Fish Accumulation**

**(A) Catfish studies**

- (1) "Catfish Tissue Residue Levels following exposure to 14C CIPL"; Smith, K.S. and Merricks, D.L. [the report by Cannon Laboratories (1/30/76) is attached to Ref #5 (pg 63)]

**Experimental:**

After a 2-week holding period small channel catfish 3-5 inch in length (80 per tank) were exposed 28 days to ring-labelled (14C) CIPL at concentrations approximately 0.07 or 0.7 ppm. The exposure system was static; the 29-gallon tank contained aerated tap-water and Keo sandy loam soil [48.4% sand; 46.4% silt; 5.2% clay; 0.8% O.M.; CEC 6.7 MEQ/100 gm; pH 5.8]. The labelled CIPL was added in a layer (ca 1-cm) of spiking soil to the Keo-layer (ca 5-cm). Spiking was equivalent to an application rate of either 0.4 lb ai/acre or 4.0 lb ai/acre.

**Depuration:** following the 28-day exposure surviving fish were maintained, with periodic sampling, for 14-days in a pesticide-free, flow through system (7.5 liters/hr).

**Analysis:** periodic samples were taken of the soil, water, and fish. The assays (LSC) had CIPL (14C) sensitivities as follows: 0.002 ppm in water; 0.008 ppm soil; 0.008 ppm tissue. Recovery from tissue was ca 90%.

**Summary of data:**

**14C Distribution (ppm); Excerpts Tables I, II and III**

Exposure* Days	0.4 lb/acre				4.0 lb/acre			
	Edible	Viscera	solv.	soil	Edible	Viscera	Solv.	Soil
1	2.13	16.29	-	-	26.10	78.34	-	-
3	3.26	26.28	-	-	18.81	114.97	-	-
7	0.10	3.59	0.07	0.23	7.73	82.74	0.60	1.70
14	0.09	1.27	0.04	0.30	0.78	38.25	0.68	2.54
21	0.05	0.78	0.07	0.36	0.59	12.15	0.72	2.53
28	0.06	2.36	0.06	0.20	0.79	27.18	0.74	3.45

\*The system was aged before the fish were added. The spiked soil was aged dry for 48-hrs and then under 50 cm of water for 2 weeks. During this time the CIPL residues averaged 0.04 and 0.44 ppm in water and 0.27 and 2.56 ppm in the soil.

Data comments:

Residues peak within 3-days and decline to a minimum by the 3rd weeks. Depuration was most rapid at the higher exposure (0.70 ppm) at lower level (0.07 ppm) residue half-life was 2-week in edible tissues.

Conclusion:

Data indicates accumulation in the food-web unlikely; accumulation factors, ca 1.0 (edible) and ca 40 (viscera).

- (2) "Qualitative Investigation of CIPL Metabolites in Catfish"; EGKE, G.G. [Ref 5(pg 46); Br. 20348 (6/11/76); As 09529 (9/21/76)]

Experimental:

The characterization work is limited to residues in edible tissue. The work was done with the small channel catfish which were subjected to the CIPL exposure described above [see(1)]. The residues were separated into three fractions as follows:

- (a) Insolubles (11% of the activity); obtained by homogenizing tissue samples with acetonitrile and a further extraction of the insolubles with hexane-acetonitrile (1-1). The hexane soluble lipids (1% of the activity) were not further studied. The acetonitrile solubles (88% of the activity) after evaporating the acetonitrile (0.2% activity loss), were soluble in either water or methylene chloride.
- (b) Water solubles (activity 62%)
- (c) Methylene chloride soluble (activity 26%)

<sup>zation</sup>  
Characteristics:

- (a) Insoluble (11%); an enzymatic hydrolysis (50 mg glucuronidase, 50 mg

23

Pronase, 10-mls acetate buffer at pH 5, were held 4-days at 38<sup>37</sup>°C) left about 1.8% of the activity insoluble. The solubilized activity (9%) was partitioned with methylene chloride (see fig.4) and the extracted activity (3.2%) was separated into fractions (7) with "biobeads"; biobead fractions (3) were then chromatographed (TLC/autoradiograph) Although much of the activity was not satisfactorily resolved, fractions (spots) were found with R<sub>f</sub> values approximating:

- (i) isopropyl 3-chloro-4-hydroxycarbanilate (compound II)
- (ii) 3-chloro-4-hydroxyactanilide (VI)
- (iii) 3-chloroacetanilide (VII)

The activity remaining in the water portion after enzymatic hydrolysis and extraction was about 5.5%.

- (b) Water solubles (ca 62%); these solubles were subjected to repeated enzymatic hydrolysis, a methylene chloride extraction following each hydrolysis. The extracted activity (ca 41%) was passed through "biobeads" to obtain further fractions. The "biobead" fractions were then chromatographed (TLC/autoradiograph). TLC spots were found with R<sub>f</sub> values approximating:

- (i) compounds II and VI (see a above)
- (ii) 2-propyl 3'-chlorocarbanilate (compound III)

The activity remaining in the water phase after hydrolysis (enzymatic) and extraction was about 16%.

- (c) Methylene chloride solubles (ca 2.6%); this fraction like the methylene extracts of the water solubles (b) and insolubles (a) was also separated with biobeads into fractions (7). Three of these fractions (ca 14.5%) were chromatographed (TLC/autoradiograph) and other aliquots were subjected to hydrolysis (enzymatic and Bleidner). The chromatographs indicated:

- (i) Compounds II, VI, VII (see a, above)
- (ii) also CIPC

Activity remaining in the water phase following the hydrolysis approximated 5%.

Summary of the data:

The total residues present at 28 day in edible catfish tissue [see 33.3(A)] approximated 0.8 ppm; the compounds shown present are approximately as follows:

- 10% CIPC
- 3% isopropyl 3-chloro-4-hydroxycarbanilate
- 0.5% 1-hydroxy-2-propyl 3'-chlorobanilate

- 18.0%; 3-chloro-4-hydroxyacetanilide
- 1.0%; 3-chloroacetanilide
- 11.%; compounds which were not identified,  $\gamma$ (8%) and  $\Sigma$ (3%).
- 27%; characterized as water solubles.
- 1%; characterized as hexane solubles
- 2%; characterized as insolubles.
- < 6%; TLC fractions (CA 12) present in amounts of less than 0.5% which were not identified.
- \*20%; activity not accounted for.

Conclusion (1 and 2):

- (a) Under the old criteria the catfish data is acceptable; residue characterization was not a requirement when the accumulation factors were small. In this study the viscera factor is less than 50.
- (b) However the data does not meet the current requirements; both the amount and identity of the residues in the whole fish, edible tissue, and viscera are needed.

(B) ~~(C)~~ Bluegill sunfish studies

- (1) "Report; Bluegill Sunfish Tissue Residue Levels Following Exposure to 14C-CIPL"; Smith, S.S. and Merricks, D.L. [the report by Cannon Laboratories (6/25/76) is attached to Ref #7(pg 84); as 095292 (9/21/76)]

Experimental:

After a one-week holding period small sunfish 2-3 inches in length (100 per tank) were exposed over a 28-day period to ring-labelled (14C) CIPL. The exposure was made in a large (30L) flow through system (7.5 liter/hr) at CIPL levels of either 0.01 or 1.0 ppm.

Depuration: following the 28-day exposure surviving fish were maintained, with periodic sampling, in a pesticide-free flow through systems (7.5 liters/hr).

Analysis: te assays(LSC) were sensitive at the 0.01 ppm exposure level to 0.008 ppm of CIPL in either water or fish. At the 1.0 ppm exposure level the sensitivity varied from 0.024 ppm (water) to 0.234 ppm (tissue).

- (2) "Qualitative Investigation of CIPL Metabolites in Bluegill Sunfish"; Ecke, G.G. [Ref 7(pg 84); BR 203.5A (7/15/76); As #095292 (9/21/76)]

Summary of data:  
 14C-CIPL Residues in Edible Tissue (ppm)

Days	0.01 PPM Level		1.0 PPM Dose Level	
	Tissue	Water	Tissue	Water
Exposure				
1	0.149	0.01	11.288	1.01
3	0.133	0.01	13.549	1.01
7	< 0.008*	0.01	7.752	0.85
14	0.088	0.01	10.903	0.85
21	0.097	0.01	11.456	0.92
25	0.204	-	16.922	-
28	0.424	0.01	17.573	0.89
Withdrawal				
1	0.054	-	1.201	-
3	0.016	-	0.968	-
7	0.032	-	1.740	-
14	0.018	-	0.489	-

\* The detection limit is 0.008 ppm.

Summary and conclusion (1)

The data indicates accumulation in the food-web is unlikely. Although the residues do not definitely plateau the accumulation factor (edible tissue) is less than 43. Further, the residue-decline during withdrawal is rapid [see also (2)]

(2) "Qualitative Investigation of CIPL Metabolites in Bluegill Sunfish"; Ecke, G.G. [Ref 7(pg 84); BR 20315A (7/15/76); As #95292(9/21/76)]

Experimental:

Characterization work is limited to residues in the edible tissue of fish obtained on the 28th day of the 1.0 ppm exposure, described above [see (1)]. The residues were separated into three fractions as follows:

(a) Insolubles (1% of the activity); obtained after homogenizing the tissue with acetonitrile and further extractions with both hexane and acetonitrile-hexane(1:1). The phases were separated and cleaned-up with back-partitioning. The hexane soluble lipids (1% activity) were not further studied. After evaporation of acetonitrile the residues (98% activity) was soluble in either water or methylene chloride.

(b) Water solubles (activity 6%)

- (b) Water solubles (6%); following an enzymatic hydrolysis [see (1)] and methylene chloride extraction the extracted activity was further separated, using biobeads, into fractions (7). Chromatographs (TLC/autoradiograph) of the principal fractions (4.8% activity) indicate the following metabolites; identified in the summary:  
 Compound II (2.46%)  
 Compound VI (0.36%)  
 Unidentified TLC Fractions (0.03%)  
 Unidentified water solubles (0.5%)

- (c) Methylene chloride solubles (ca 90%); biobeads were used to separate fractions (7). Chromatographs as in (b) were made of cuts #1-2 (3.1%); cut #3 (8.9%); cuts #4-6 (72/s) the compounds identified were:  
<sup>38.1</sup>  
 CIPL (38.1%)  
 Compound II (5.81%)  
 Unidentified TLC fractions ((1.19%)  
 Unidentified hexane solubles (1.0%)

Summary

- (a) The study accounts for only about one-half of the activity in the edible residues (18 ppm).

Compound	%	No.
CIPL	38.1	-
3-chloro-4-hydroxycarbanilate	9.3	II
3-chloro-4-hydroxyacetanilide	0.4	VI
Unidentified; TLC fractions	2.0	-
hexane solubles	1.0	-
water solubles	0.5	-
insolubles	1.0	-

- (b) Data on the nature of the residues in whole fish and viscera are not reported.

Conclusion (1 and 2):

Although the data indicates bluegills do not metabolize CIPL as well as do catfish the conclusions are the same:

- (a) Under the old standards the data is acceptable since characterization of the residues was not required when the accumulation factors were small; the edible tissue factor is ca 43. in bluegills.
- (b) But the data is not acceptable under the new standards which require an evaluation of the residues both quantitatively and qualitatively in the whole fish, edible tissue, and viscera.

4.0 Summary and Conclusions:

4.1 Hydrolysis:

- (a) data previously reviewed (8/75) shows half-life ranging from 12-days (distilled) to 32-days in canal water; our file indicates petition 1F1120 contains data on the hydrolysis products. The study does not meet either the old or new criteria.
- (b) The need for additional hydrolysis data was not included in our recent reviews (8/75 and 11/75).

4.2 Photolysis:

- (a) The solution data (see 3.1) is acceptable. CIPE's half-life ranged from 80-140 hours (25%) in distilled water; it varied somewhat with concentration. The principal photoproduct is identified; the minor products are characterized; CIPE is shown subject to photosensitization.
- (b) Photodegradation data on soil which is required under both the new and old guidelines has not been submitted or referenced.
- (c) Vapor-phase photoproducts; the need for this data is contingent on the re-entry requirement and the review by toxicology.

4.3 Leaching

- (a) An aged leach study has not been submitted and is required by the new guidelines.
- (b) The referenced studies (#19, #20, #21, #22) were found acceptable in our review (11/95); CIPE's mobility on 5-soils (loam; clay loams; silt clay loam; muck) ranged from low to moderate.
- (d) A review of field-leach data (8/95) indicates CIPE leaches very little.

4.4 Aerobic/Anaerobic (3.2)

- (a) The studies were short but otherwise acceptable. The aerobic data (13 weeks) indicates the CIPE loss ca 85% (not 90% as required) with a decline rate of ca 6.5%/week (see 3.2 (B)). About 61% was bound and characterized (3.2(c)); see also the rotational study (3.2). The  $^{14}\text{C}$ - $\text{CO}_2$  loss was ca 13%; degradates accounting for the loss were presumably soil bound.

(b) Reviewed data (8/75) indicates degradation does not result in the formation of azo-compounds.

4.5 Microbial studies; the data reviewed (6/22/75) show CIPC and its primary soil metabolite (3-chloroaniline) inhibitory (ca 25 ppm) to nitrification (genus nitrosoma). However various species were capable of using CIPC as the only source of carbon. *But not accept under N. G. 1's*

4.6 Volatility and Dislodgable residues (new reg's)

(a) A flask <sup>16s</sup> study previously reviewed (8/75) provides vapor-loss data (416/acre) from four soils, but data under actual use conditions has not been submitted; nor has data on the dislodgable residues.

(b) Our need for additional studies is conditional to the re-entry requirement and the toxicology review.

4.7 X Rotational Crops (3.3); the data indicates a field study will be required.

(a) CIPL residues were determined (GLC/EC) in sugarbeet root (0.70 ppm), lettuce (0.16 ppm), wheat straw (0.57 ppm) and grain (0.22 ppm). Residues based on 14C (LSC) were lower; the analytical discrepancy is attributed to; "contamination of the growing area." Since the growing <sup>area</sup> includes the soil, soil bound CIPC residues (cold) might account for the analytical discrepancy.

(b) Characterization was limited to SB-root residues (0.70 ppm); about 74% was not extracted; ca 24% remained water soluble following a methylene chloride partition; ca 2% was identified.

4.8 Tank Mix (3.4)

The data shows increases in the persistence of both CIPL and the propose tank mix herbicides. The half-life data, however the half-life data of neither CIPC nor the interaction herbicides exceeds 18 weeks. The need for additional data is not indicated.

4.9 Fish studies (3.5; A,B)

(a) Under the old guidelines the data would be acceptable; but the data does not meet the current requirements for the amount and identity of the residue in whole fish, edible tissue, and viscera.

(b) Accumulation in the food chain appears unlikely:

(i) Accumulation factor are small in both studies, edible tissue ca 1.0 (catfish) and ca 43 (bluegills); viscera ca 40 (catfish), viscera data has not been submitted for bluegills.

(ii) Depuration is rapid in both studies.

(c) Characterization work was limited to the edible tissue in both studies.

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5.0 Recommendations  
This section void. (type but do not send out)

5.1 We do not concur.

5.2 The following studies required by the old draft guidelines have not been submitted. The additional data required by the new guidelines is indicated below (5.4).

- (1) Hydrolysis: the study (Sect. D petition 1F119) included in a previous submission is not sufficient. Data is needed at different pHs (acid, basic, neutral); also data on the nature of the hydrolysis products and material balance.
- (2) Photodegradation on soil.
- (3) Aged leaching.
- (4) Rotational crops: the submitted study (Ref #41) indicates residues which indicate the need for actual field studies using un-labelled CIPC.

5.3 The following studies are needed under the current guidelines.

- (1) Hydrolysis, the data above [5.2(1)]; also data at two concentrations and two temperatures (~~see 5.4(1)~~ see 5.4(1)).
- (2) photodegradation in soil (~~see 5.4~~ (see 6.15)).
- (3) Vapor-phase photolysis also volatility and dislodgable residues; the need for this data is contingent to the review by toxicology and the re-entry requirement. see 6.15.
- (4) Aged leaching (~~see 5.4(2)~~ see 5.4(2)).
- (5) Rotational crop study; see above (5.2(4)) and also 5.4(4).
- (6) Fish accumulation; the submitted studies (Refs 5, 5a, 6, 7) do not include as required, data on the amount and identity of the residues in soil, whole fish, edible tissue and viscera at each sampling interval ~~see 6.15~~ (see 6.15).

5.4 <sup>(7) Microbial</sup> Description of the currently required studies:

(1) Hydrolysis

Studies are conducted in darkness using radioisotopic or other comparable techniques at different pH values (acidic, neutral or basic) at two concentrations, and two temperatures. Aliquots in duplicate should be taken at four sampling time intervals, with at least one observation made after one-half of the pesticide is hydrolyzed or thirty days, whichever is shorter. A material balance, half-life estimate and identification of degradation

products for the pesticide must be provided. Studies in distilled water provide an upper limit estimate for persistence of pesticides in the aquatic environment. Hydrolysis in natural waters may be carried out to supplement studies in distilled water.

(2) Leaching. Leaching through soil is dependent upon pesticide formulation, physical and chemical properties of pesticide and soil and environmental conditions. Add pesticide to soil(s) corresponding to the highest recommended rate for a single application and study leaching using radioisotopic or comparable techniques to provide a quantitative estimate of mobility in soil. Each study will include soils as sand (agricultural), sandy loam, silt loam, clay or clay loam having a pH range of 4 to 8 with at least one soil having an organic matter content less than one percent. Use a minimum of four soils to study pesticide leaching and elute each immediately with twenty acre-inches water. Use one of the above soils to study leaching of pesticide residues wherein the pesticide is aged in soil under aerobic conditions [see 162.79 (d)(3)(ii)] for thirty days prior to eluting with one-half acre-inches water per day for forty-five days. Two basic techniques for measuring leaching are soil column and soil thin-layer chromatography (soil TLC). For acceptable procedures for this test, see Appendix Item 9.

(4) Field dissipation. (i) General. A field dissipation study under actual use conditions is required. Decline curves under field conditions define the duration of potential hazards. Dissipation may decrease potential hazard of reentry into the treated area, residues in rotational crops, and residues in the food web, and may result in loss of usable land and water resources through degradation processes in the treated area, or may increase potential hazards in non-treated areas through mobility. Continue analyses until a ninety percent loss of the pesticide occurs or until patterns of formation and decline of degradation products are established, or to the maximum time specified in (ii) (A) through (F) and (iii)(A) and (B). Sampling times include pre-application, day of application, and shortly post-application for each single or multiple application. The collection of succeeding samples is dependent upon degradation and metabolism characteristics, and potential for reentry. Identification of residues comprising more than ten percent of initial application or 0.01 ppm is needed for the registrant to construct decline curves of residues in foliage, litter, soil, and water. For supplemental information for these tests, see Appendix Item 13.

(ii) Terrestrial. Terrestrial field dissipation tests are specified below. If multiple applications are anticipated, then this use pattern must be reflected in the study.

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(A) Field and vegetable crop uses. Take soil samples in increments to a depth of 12 inches from sites in four agricultural use areas for a maximum test duration of eighteen months.

6.0

Conclusions

The currently submitted or referenced data are inadequate to form and opinion on unreasonable adverse effects on the environment.

7.0

Recommendations

No recommendation, since the data is inadequate to form an opinion.

The following data are inadequate, for the following specific reasons.

*canal + distilled water*

Hydrolysis study conducted at two pHs, whereas 3 pHs (acidic, neutral, and basic), 2 temperatures and 2 concentrations are required.

Photodegradation study on soil is not submitted or referenced.

The field dissipation study is not submitted or referenced.

Rotational crop residue study under field conditions is required, in order to determine a time interval sufficient to ensure that subsequent crops do not contain residues. The currently submitted data demonstrates residues in rotational crops.

For registration, the following studies are required under current operating procedures. Such studies must be submitted or referenced.

7.1

A hydrolysis study using radioisotopic or comparable technique is required. Acidic, neutral, and basic pH's are used. Two concentrations and two temperatures are required. Aliquots in duplicate should be taken at four sampling intervals with at least one observation made after one-half of the pesticide is hydrolyzed, or 30 days, whichever is shorter. A material balance, half-life estimate, and identification of degradation products must be provided. Concentrations should approximate use rate and TOX use rate.

*Criteria*

*AG 1*  
*Soil*

7.2

A photodegradation study in water is conducted at pH of maximum stability. Conduct photodegradation study using radioisotopic or comparable techniques at one concentration (approximately use rate) under natural or simulated (greater than  $280 \times 10^{-9}$  meters wavelength) sunlight. Material balance, half-life estimate and identification of photoproducts must be provided. Rate studies are conducted in distilled or deionized water and sampling should continue

*Also Soil*

until twenty percent degradation is observed and for thirty days to identify photoproducts. A comparable photodegradation study on soil is required.

7.3

Aerobic and anaerobic soil metabolism study is required using a sandy loam, loam, silt loam, or other textured soil appropriate to the intended application sites. Radiolabeling in one or more positions in the pesticide molecule is required to assure adequate coverage of chemical transformations. Where radiolabeling will be of little benefit, comparable techniques are required. Residues comprising more than two percent of initial application or 0.01 ppm should be identified. A material balance, including nonextractable residues, must be provided. The experimental dose rate should approximate field application rate. Treated soil should be maintained at temperatures of 18 to 30°C at or below 75% of 0.33 bar moisture. Data are collected until a ninety percent loss of the pesticide occurs and until patterns of formation and decline of metabolic products are established, for a maximum test duration of one year. Preferred sampling times are at pretreatment, 0, 1, 2, 4, and 7 days, 2 and 3 weeks, and 1, 2, 3, 4, 6, 9 and 12 months.

For the anaerobic portion of the study, an aliquot of treated soil at the thirty-day interval is obtained from the aerobic soil study, and anaerobicity is established by either waterlogging or purging with inert gases. Preferred sampling intervals are 30 and 60 days after anaerobicity has been established.

7.4

#### Microbial Metabolism

Effects of microbes and pesticides: Impact of microbes on pesticide transformation include comparisons of metabolic processes under sterile and nonsterile conditions during a thirty-day period. Preferred sampling intervals are 1, 3, 7, 14, 21, and 30 days but other intervals may be appropriate. Acceptable soil sterilization methods are heat or high energy ionizing irradiation. Attempts should be made to identify organisms responsible for degradation. For organisms which are difficult to identify, family names will be sufficient. Isolates that cannot be identified to family level must have descriptive characteristics which can be substituted for generic classification. Alternatively, studies utilizing pure or defined and characterized mixed cultures of bacteria, algae and/or fungi are adequate.

#### Effects of Pesticides on Microbes

Data on effects of pesticides on microbes are obtained from studies of effects on microbial functions or microbial populations. Study of effects on microbial functions or microbial populations. Study of effects on microbial function constitute a more direct approach, and are preferred to studies of effects on populations. Some effects

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cannot be measured directly and population studies may be the only recourse. When the functional approach is chosen, the effects on nitrogen fixation, nitrification, cellulose, starch and protein degradation are required. When the population approach is chosen, effects on pure or mixed culture populations representative microorganisms from soil or water or obtained from culture collections are required.

Appropriate organisms include free living nitrogen-fixing bacteria and blue-green algae such as Azotobacter, Clostridium, and Nostoc, and nitrifiers such as Nitrosomonas and Nitrobacter. For cellulose, starch and protein degradation, include at least one each of soil bacteria, actinomycetes, and molds such as Bacillus, Pseudomonas, Arthrobacter, Cellulomonas, Cytophaga, Streptomyces, Penicillium, Flavobacterium, Trichoderma, Aspergillus, Chaetomium, and Fusarium. Animal or plant pathogens and indicators of fecal pollution are unsuitable.

7.5

A leaching study using radioisotopic or comparable techniques is required. A minimum of four soils are used, including soils such as sand (agricultural), sandy loam, silt loam, clay or clay loam having a pH range of 4 to 8 with at least one soil having an organic matter content less than one percent. The pesticide is added to soil corresponding to the highest recommended rate for a single application. Each soil is immediately leached with the equivalent of twenty acre-inches of water. In addition, one of the above treated soils is aged for 30 days under aerobic conditions prior to initiation of leaching, which is at the rate of equivalent one-half acre-inch of water per day for forth-five days. A material balance depth of leaching, and quantity and identify of the pesticide and its degradation products or metabolites must be provided.

9.6

A field dissipation study under actual use conditions is required. Analyses are continued until a ninety percent loss of the pesticide occurs or until patterns of formation and decline of degradation products are established or to a maximum test duration of eighteen months. Soil samples are taken in increments to a depth of 12 inches from sites in four agricultural use areas. Sampling times include pre-application, day of application, and shortly post-application. Succeeding samples are dependent upon degradation and metabolism characteristics.

Identification of residues comprising more than ten percent of initial application or 0.01 ppm is needed to construct decline curves of residues in soil.

*long term studies*

9.7

A rotational crop residue study is required to establish if pesticide residue uptake occurs in rotational crops, emergency replanting or in situations where crops receive water from treated areas. Crops that can be rotated with the treated crop in the proposed use areas must be identified. A sandy loam soil is treated with a radiolabeled pesticide at a rate equivalent of that expected under actual use conditions. Following treatment the soil is aged aerobically for a time approximating the anticipated cultural practice, for example: one year for crops rotated the following year, 120 days for crops rotated immediately after harvest and 30 days for assessing circumstances of crop failure-emergency replanting. A root crop, small grain and leafy vegetable crop are planted at the above times and periodically analyzed to maturity. When residues are found, a field study using formulated products will establish an interval when residues would not occur in subsequent crops under actual use conditions. A crop residue study under actual use conditions is required for those cultural practices where a subsequent crop is treated with the same active ingredient as the initial crop. This study is not required for a cover crop if plowed under and not grazed.

9.8

Fish residue accumulation data using radioisotopic or comparable technique are required. Two exposure systems are required: flow-through (with constant concentration of aqueous solution of pesticide) and static (with ambient concentration of residues). Bluegill sunfish are preferred in flow-through system and catfish required in the static system. For the static system treat water overlaying a sandy loam soil at the proposed applications rate and allow system to "age" for 2 to 4 weeks prior to initiation of fish exposure.

Exposure duration is 30 days with suggested sampling times at 0, 1, 3, 7, 10, 14, 22, and 30 days of exposure; while fish and water samples are taken on 0, 1, 3, 7, 10, and 14 days of withdrawal of exposure. Obtain soil and water samples prior to fish exposure interval. Determine the amount and identity of the residue in water, soil, whole body fish, edible tissue, and viscera or carcass at each sample interval.

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