

US EPA ARCHIVE DOCUMENT

8-4-87

059101

Shaughnessy No.: 059101

Date Out of EAB: AUG - 4 1987

To: Dennis Edwards  
Product Manager # 12  
Registration Division (TS-767)

From: Therese M. Dougherty, Chief  
Environmental Chemistry Review Section 1  
Exposure Assessment Branch  
Hazard Evaluation Division (TS-769-C)

*THD*

Attached, please find the EAB review of...

Reg./File # : 464-404  
Chemical Name: Chlorpyrifos  
Type Product : Insecticide  
Product Name : DURSBAN/LORSBAN  
Company Name : Dow Chemical  
Purpose : Review fish accumulation study as required by Registration Standard.

Action Code: 605 EAB #(s): 70259  
Date Received: 2/12/87 TAIS Code: 108  
Date Completed: AUG - 4 1987 Total Reviewing Time: 3.0 days  
Monitoring study requested: \_\_\_\_\_  
Monitoring study voluntarily: \_\_\_\_\_

Deferrals to: \_\_\_\_\_ Ecological Effects Branch  
\_\_\_\_\_ Residue Chemistry Branch  
\_\_\_\_\_ Toxicology Branch

1.

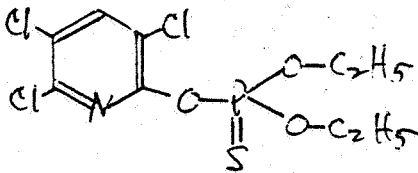
1. CHEMICAL:

Common Name- Chlorpyrifos

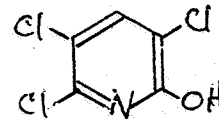
Chemical Name- O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)phosphorothioate

Trade Name- DURSBAN, LORSBAN

Chemical Structure-



Chlorpyrifos  
\* denotes <sup>14</sup>C-radiolabel



Trichloropyridinol (TCP)  
major degradate

2. TEST MATERIAL: [2,6-<sup>14</sup>C] chlorpyrifos at radiopurity of at least 98%, as determined by HPLC.
3. STUDY/ACTION TYPE: Dow Chemical is submitting a fish accumulation study (\$165-4) for review in response to the chlorpyrifos registration standard.
4. STUDY IDENTIFICATION: Bioconcentration of chlorpyrifos in Rainbow Trout (*Salmo gairdneri*, Richardson), P.G. Murphy and N.E. Lutenske, 30 Dec 1986, Dow Chemical, Project #ES-928, Acc. #400564-01.

5. REVIEWED BY:

Herbert L. Manning, Ph.D.  
Microbiologist  
EAB/HED

Signature: *Herbert L. Manning*  
Date: AUG - 4 1987

6. APPROVED BY:

Therese M. Dougherty, Chief  
Section 1  
EAB/HED

Signature: *Therese M. Dougherty*  
Date:

AUG - 4 1987

7. CONCLUSION:

Rainbow trout, in a flow-through, <sup>14</sup>C-labeled study was shown to accumulation chlorpyrifos in whole fish with BCF of 1374 and in fillets with BCF of 725. The study is acceptable.

*2*

8. RECOMMENDATION:

EAB finds the fish accumulation study acceptable and as satisfying this data requirement.

9. BACKGROUND:A. Introduction-

The chlorpyrifos Registration Standard (Guidance for Reregistration) was issued Sep 28, 1984 by the Agency. EAB's Summary Table A (Generic Data Requirements for Chlorpyrifos) from that standard is attached.

An addendum to the standard was made Oct 25, 1986 that reviewed several required studies:

- Hydrolysis- Study was accepted.
- Leaching (adsorption/desorption)- Partially satisfied requirement. Several deficiencies cited.
- Lab volatility- Several deficiencies; study unacceptable.

Chlorpyrifos is a broad spectrum insecticide that is registered on a variety of crop and non-crop uses (see Table A). Application rates range from 0.1 oz ai/A (seed treatment) to about 50 lb ai/A (certain tree fruit).

B. Directions for Use-

Not applicable. No label submitted.

10. DISCUSSION OF STUDY:A. Study Identification-

Bioconcentration of Chlorpyrifos in Rainbow Trout.

B. Materials and Methods-

Test material- Fish were exposed 30 days to an average concentration of <sup>14</sup>C -labeled chlorpyrifos of 0.30 ug/L (ppb) which is less than 1/10 of the 96-hr LC<sub>50</sub> (11 ug/L).

Test fish- Eighty-five rainbow trout, 3.5-5.0 cm long and weighing 0.6-0.7 g, were tested in each aquarium.

Dilution water- The primary source was upper Saginaw Bay of Lake Huron that was limed and flocculated (ferric chloride) before entering lab. Water is sand and carbon filtered, adjusted to about pH 8, and UV irradiated before use.

Test system- Three 40-L glass aquaria (control, exposure, and depuration) were positioned in a constant temperature water trough set at 12°C. The water dilutor system made five volume changes to each aquarium every 24-hour. The system is shown in Figure 2.

Sampling- Fish were sampled after 0.5, 1, 2, 4, 8, 15, 21, 28, and 30 days exposure to chlorpyrifos. Of the five fish taken, one was combusted for total activity in the whole fish, one separated into fillet and remainder (head, viscera, skeleton) and each combusted, two extracted for parent/degradate characterization, and one frozen for future analysis. The exposure period was extended to 30 days (from 28) because of about a 9-hour power outage on the 3rd day.

Sampling during depuration (clearance phase) was on day 1, 3, 6, 9, 12, and 16.

Analyses- Total radioactivity of water samples was determined by liquid scintillation counting (LSC). Fish tissues were combusted and the  $^{14}\text{CO}_2$  analyzed by LSC. Recovery of  $^{14}\text{CO}_2$  was 93.8%  $\pm$  4.2, and corrections were made on combustion sample sets.

For determination of parent and metabolites from water samples, extracts (Figure 3) were analyzed by HPLC. Recovery was 97.5%  $\pm$  1.25%. Similarly, fish tissue extractions (Figure 4) were analyzed by HPLC. Recovery was 116%  $\pm$  14.7%.

Modeling- The measured concentrations of  $^{14}\text{C}$ -chlorpyrifos in fish and water were evaluated using BIOFAC, stated as being one of the preferred methods of EPA for evaluating bioconcentration data.

### C. Results-

Table IV characterizes exposure water extracts. Table V shows residue levels in clearance (depuration) water. Table VII shows radioactivity in fish in exposure and clearance phases. Table IX and Table X shows characterization/identification of residues in organic extractions, in exposure and clearance fish, respectively. Table XI shows calculation of bioconcentration factors (BCF) in whole fish and fillets.

The findings may be summarized as follows:

1. The chlorpyrifos level in water extracts averaged 92.8% of the  $^{14}\text{C}$  activity in the extracts (Table IV).
2.  $^{14}\text{C}$ -residues in uptake phase in fish fillet, fish remainder, and whole fish were still increasing after 28 days- no leveling off was observed. This was also true for extracted fish. Residues in clearance phase steadily decreased (Table VII).

3. Identified metabolites were: polar metabolites 1 and 2 and trichloropyridinol (TCP). Analysis of polar metabolites 1 and 2 showed them to be conjugates of TCP. The polar metabolites accounted for 10-30% of activity and TCP about 5-20% (Table IX and X).
4. BCF for chlorpyrifos in whole fish was 1374  $\neq$  321 and for fish fillet it was 725  $\neq$  136.
5. Figure 3 shows simulation plot of chlorpyrifos in whole fish.

D. Author's Conclusion-

Using BIOFAC, a computer simulation program that employs measured concentration of a chemical in fish and water, chlorpyrifos was shown to accumulate (BCF of 1374 for whole fish) in rainbow trout and was in agreement with other reported values (468-1885\*) for chlorpyrifos.

E. Reviewer's Comments-

The study was well done and was acceptable in all aspects except one: steady-state (equilibrium) of chlorpyrifos uptake was not reached during the 30 day exposure period. The author's state that: "the estimated time to 90% of steady-state for both chlorpyrifos and total <sup>14</sup>C-residue was about 7 to 9 days." However, Table VII does not indicate that this the case.

This discrepancy notwithstanding, EAB considers the study acceptable since chlorpyrifos was shown to bioaccumulate in rainbow trout and in light of referenced data showing a BCF of up to 1885, the maximum BCF probably approaches this latter value.

11. COMPLETION OF ONE-LINER:

Not applicable.

12. CONFIDENTIAL APPENDIX:

Contains supporting information.

\* 1978. Marshall, W.K. and J.R. Roberts. Ecotoxicology of Chlorpyrifos, Subcommittee on Pesticides and Related Compounds. National Res. Council of Canada. NRCC 16079.

12. CONFIDENTIAL APPENDIX

TABLE A  
 GENERIC DATA REQUIREMENTS FOR CHLORPYRIFOS

Data Requirement	1 Composition	Use 2 Pattern	Does EPA Have Data To Satisfy This Requirement? (Yes, No or Partially)	Bibliographic Citation	Must Additional Data Be Submitted Under FIFRA Section 3(c)(2)(B)? <sup>3</sup>
<u>\$158.130 Environmental Fate</u>					
<u>DEGRADATION STUDIES-LAB:</u>					
161-1 - Hydrolysis	TGAI of PAIRA	A, B, D, F, G, H	No	-	Yes <sup>4</sup>
<u>Photodegradation</u>					
161-2 - In water	TGAI of PAIRA	A, B, D, G	No	-	Yes <sup>4</sup>
161-3 - On soil	TGAI of PAIRA	A	No	-	Yes <sup>4</sup>
161-4 - In Air	TGAI of PAIRA	A, B, F, G	No	-	Yes <sup>4</sup>
<u>METABOLISM STUDIES-LAB:</u>					
162-1 - Aerobic Soil	TGAI of PAIRA	A, B, G	Yes	00073059, 000095381 00025619	No
162-2 - Anaerobic Soil	TGAI of PAIRA	A	Yes	00025619	No
162-3 - Anaerobic Aquatic	TGAI of PAIRA	D, G	No	-	Yes <sup>3</sup>
162-4 - Aerobic Aquatic	TGAI of PAIRA	D	No	-	Yes <sup>3</sup>
<u>MOBILITY STUDIES:</u>					
163-1 - Leaching and Adsorption/Desorption	TGAI of PAIRA	A, B, F, G, H	No	-	Yes <sup>4</sup>
163-2 - Volatility (Lab)	TEP	A, F, G, I*	No	-	Yes <sup>4</sup>
163-3 - Volatility (Field)	TEP	A, F, I	No	-	Yes <sup>4</sup>

\* Plus commercial establishments, pet/animal housing.



TABLE A  
 GENERIC DATA REQUIREMENTS FOR CHLORPYRIFOS

Data Requirement	Composition	1	Use 2	Does EPA Have Data To Satisfy This Requirement? (Yes, No or Partially)	Bibliographic Citation	Must Additional Data Be Submitted Under FIFRA Section 3(c)(2)(B)?3
<u>§158.130 Environmental Fate (continued)</u>						
<u>DISSIPATION STUDIES-FIELD:</u>						
164-1 - Soil	TEP		A, B, G, H	No	-	Yes3
164-2 - Aquatic (Sediment)	TEP		D	No	-	Yes3
164-3 - Forestry	TEP		G	No	-	Yes3
164-4 - Combination and Tank Mixes			-	N/A	-	No5
164-5 - Soil, Long-term	TEP		A	Yes	00025619, 00095381 00073059	No6
<u>ACCUMULATION STUDIES:</u>						
165-1 - Rotational Crops (Confined)	PAIRA		A	No	-	Yes3
165-2 - Rotational Crops (Field)	TEP		A	No	-	Yes3
165-3 - Irrigated Crops	TEP		D	No	-	Yes3
165-4 - In Fish	TGAI or PAIRA		A, B, D, G, H	No	-	Yes3
165-5 - In Aquatic Non-Target Organisms	TEP		A, B, D, G, H	No	-	Yes3

2

TABLE A  
GENERIC DATA REQUIREMENTS FOR CHLORPYRIFOS

\$158.130 Environmental Fate  
(continued)

1. Composition: TGAI = Technical grade of the active ingredient; PAIRA = Pure active ingredient, radiolabelled; TEP = Typical end-use product.
2. The use patterns are coded as follows: A=Terrestrial, Food Crop; B=Terrestrial, Non-Food; C=Aquatic, Food Crop; D=Aquatic, Non-Food; E=Greenhouse, Food Crop; F=Greenhouse, Non-Food; G=Forestry; H=Domestic Outdoor; I=Indoor.
3. Data must be submitted no later than OCT 1980.
4. Data must be submitted no later than MAR 1985.
5. This Guidance Document deals only with single active ingredients.
6. The data which were submitted for aerobic soil metabolism meet this requirement.

---

Page \_\_\_\_\_ is not included in this copy.

Pages 10 through 19 are not included.

---

The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
  - FDRA registration data.
  - The document is a duplicate of page(s) \_\_\_\_\_.
  - The document is not responsive to the request.
- 

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

---

Shaughnessy No: 059101

Date Out of EAB: MAY 19 1986

To: L. Schnaubelt  
Product Manager 12  
Registration Division (TS-767)

*SM*

From: Samuel M. Creeger, Chief  
Environmental Chemistry Review Section 1  
Exposure Assessment Branch  
Hazard Evaluation Division TS-769c

Attached, please find the EAB review of:

Reg./File # : 464-404

Chemical Name: Chlorpyrifos

Type Product : Insecticide

Product Name : Dursban/Lorsban

Company Name : Dow Chemical

Purpose : Protocol: fish accumulation in bluegill sunfish.

Date In: 5/7/86

Action Code: 352

Date Completed: 5/15/86

EAB #(s) : 6586

Reviewing Time: 0.5 day

Deferrals to:

Ecological Effects Branch

Residue Chemistry Branch

Toxicology Branch

Monitoring study requested by EAB:

Monitoring study voluntarily conducted by registrant:

*20*

*Pages 6-11 contain data submitted by Dow Chemical Co.*

1.

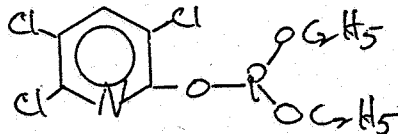
1. CHEMICAL:

Common Name- chlorpyrifos

Chemical Name- O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate

Trade Name- Dursban/Lorsban

Chemical Structure-



2. TEST MATERIAL: Pyridine-ring labeled <sup>14</sup>C-chlorpyrifos at exposure concentration of 0.3 to 0.5 ug/L (ppb).

3. STUDY/ACTION TYPE: Dow chemical is requesting a review of a protocol of a fish accumulation study using bluegill sunfish.

4. PROTOCOL IDENTIFICATION: Bioconcentration of Chlorpyrifos in Bluegill (*Lepomis macrochirus* Rafinesque), Preliminary Copy, File No. ES-DR-043-4946-5.

5. REVIEWED BY:

Herbert L. Manning, Ph.D.  
Microbiologist  
EAB/HED

Signature: *Herbert L. Manning*

Date: 19 May 1986

6. APPROVED BY:

Samuel M. Creeger  
Chief, Section 1  
EAB/HED

Signature: *Samuel M. Creeger*

Date: MAY 19 1986

7. CONCLUSIONS:

The proposed protocol is not acceptable (see RECOMMENDATION for specific comments).

21

8. RECOMMENDATION:

EAB finds the protocol for the fish accumulation study unacceptable for the following reasons:

- 1) The strategy to terminate the exposure part of the study if the three consecutive samples of the first 48 hours show plateauing of accumulation may be misleading and does not follow our guidelines. See Section 10 for more detail.
- 2) The residues in frozen samples must be shown to be stable for the storage period.

The following sampling schedule for fish and water is recommended:

Exposure days: -1, 1, 3, 7, 10, 14, 21, and 28

Depuration days: 1, 3, 7, and 14.

9. BACKGROUND:A. Introduction

See Section 3 of this review.

B. Direction for Use

See attached protocol.

10. DISCUSSION OF PROTOCOL:

The protocol is not acceptable for two reasons:

- 1) We do not concur with terminating the study if three consecutive analyses of fish (within the first 48 hours of the study) show accumulation to plateau. Such early plateauing does not necessarily mean equilibrium of chlorpyrifos residues between the fish and the water has been reached. Residue accumulation in the fish may show a plateau early in the study but then climb to a second, higher plateau during further exposure. This would be due to partitioning or metabolism of the chlorpyrifos that did not occur within the first 48 hours while the fish (i.e., its biochemistry) was adjusting to the presence of the chlorpyrifos.
- 2) Since some samples will be kept in frozen storage before being analyzed, storage stability data will be needed showing the chlorpyrifos residues to be stable during this period.

11. COMPLETION OF ONE-LINER:

Not applicable.

12. CONFIDENTIAL APPENDIX:

Contains the protocol.

23

12. CONFIDENTIAL APPENDIX

24



HEALTH AND ENVIRONMENTAL SCIENCES  
THE DOW CHEMICAL COMPANY  
PROTOCOL

MAMMALIAN AND ENVIRONMENTAL TOXICOLOGY  
1702 BUILDING, MIDLAND, MICHIGAN 48674

---

TITLE: BIOCONCENTRATION OF CHLORPYRIFOS IN BLUEGILL (LEPOMIS MACROCHIRUS  
RAFINESQUE)

DATE: FILE NUMBER: ES-DR-043-4946-5

PROPOSED STARTING DATE: 5/86 PROBLEM NUMBER: 191-3100221

ESTIMATED DATE FINAL REPORT: 8/86 SPONSOR: R. F. Bischoff  
Ag. Products  
9008 Bldg.

25

---

Page \_\_\_\_\_ is not included in this copy.

Pages 26 through 30 are not included.

---

The material not included contains the following type of information:

- Identity of product inert ingredients.
  - Identity of product impurities.
  - Description of the product manufacturing process.
  - Description of quality control procedures.
  - Identity of the source of product ingredients.
  - Sales or other commercial/financial information.
  - A draft product label.
  - The product confidential statement of formula.
  - Information about a pending registration action.
  - FIFRA registration data.
  - The document is a duplicate of page(s) \_\_\_\_\_.
  - The document is not responsive to the request.
- 

The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

---