

US EPA ARCHIVE DOCUMENT

Shaughnessy No.: 0591 01

Date Out of EAB: OCT 25 1986

To: Jay Ellenberger
Product Manager 12
Registration Division (TS-767)

From: Emil Regelman, Supervisory Chemist
Review Section #3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769)



Attached, please find the EAB review of...

Reg./File # : 464-404
Chemical Name: Chlorpyrifos
Type Product : Insecticide
Product Name : Dursban
Company Name : Dow Chemical U.S.A.
Purpose : Addendum to a Standard

Action Code(s): 616 , _____ EAB #(s): 6285 & 6243
Date Received: 02/04/86 & 01/14/86 TAIS Code: 44
Date Completed: 10-23-86 Monitoring submitted: _____
Total Reviewing Time: 3.0 days Monitoring requested: _____

Deferrals to: _____ Ecological Effects Branch
_____ Residue Chemistry Branch
_____ Toxicology Branch

6243

REGISTRATION DIVISION DATA REVIEW RECORD

Confidential Business Information - Does Not Contain National Security Information (E.O. 12065)

12866

1. CHEMICAL NAME

rhlor...for

1-14-86

2. IDENTIFYING NUMBER 464-404	3. ACTION CODE 616	4. ACCESSION NUMBER 260794	TO BE COMPLETED BY PM
			5. RECORD NUMBER 165367
			6. REFERENCE NUMBER
			7. DATE RECEIVED (EPA)
			8. STATUTORY DUE DATE
			9. PRODUCT MANAGER (PM) Ellenberger
			10. PM TEAM NUMBER 12

14. CHECK IF APPLICABLE

- Public Health/Quarantine
- Minor Use
- Substitute Chemical
- Part of IPM
- Seasonal Concern
- Review Requires Less Than 4 Hours

AH

TO BE COMPLETED BY PCB

- 11. DATE SENT TO HED/TSS
01-14-86
- 12. PRIORITY NUMBER
50
- 13. PROJECTED RETURN DATE
03-21-86

15. INSTRUCTIONS TO REVIEWER

- A. HED Total Assessment - 3(c)(5)
- Incremental Risk Assessment - 3(c)(7) and/or E.L. Johnson memo of May 12, 1977.
- C. BFSD
- D. TSS/RD
- E. Other
- B. SPRD (Send Copy of Form to SPRD PM)
- Chemical Undergoing Active RPAR Review
- Chemical Undergoing Active Registration Standards Review

F. INSTRUCTIONS

16. RELATED ACTIONS

17. 3(c)(1)(D)

- Use Any or All Available Information
- Use Only Attached Data
- Use Only the Attached Data for Formulation and Any or All Available Information on the Technical or Manufacturing Chemical.

18. REVIEWS SENT TO

- TB
- EEB
- EF
- PL
- RCB
- EFB
- CH
- BFSD

19. To	TYPE OF REVIEW	NUMBER OF ACTIONS							
		Registration	Petition	EUP	SLN	Sec. 18	Inert	MNR. USE	Other
HED	TOXICOLOGY								
	ECOLOGICAL EFFECTS								
	RESIDUE CHEMISTRY								
	X ENVIRONMENTAL DATA	1							
RD/TSS	CHEMISTRY								
	EFFICACY								
	PRECAUTIONARY LABELING								
BFSD	ECONOMIC ANALYSIS								

- 20. Label Submitted with Application Attached
- 21. Confidential Statement of Formula
- 22. Representative Labels Showing Accepted Uses Attached
- 23. Date Returned to RD (to be completed by HED)
- 24. Include an Original and 4 (four) Copies of This Completed Form for Each Branch Checked for Review.

2

REGISTRATION DIVISION DATA REVIEW RECORD
 Confidential Business Information - Does Not Contain National Security Information (E.O. 12065)

6285
 13057
 2-4-86

1. CHEMICAL NAME <i>Citlorpyrites</i>			
2. IDENTIFYING NUMBER <i>464-404</i>	3. ACTION CODE <i>616</i>	4. ACCESSION NUMBER <i>261112</i>	TO BE COMPLETED BY PM
			5. RECORD NUMBER <i>166809</i>
			6. REFERENCE NUMBER <i>10</i>
			7. DATE RECEIVED (EPA) <i>1-31-86</i>
			8. STATUTORY DUE DATE
			9. PRODUCT MANAGER (PM) <i>Ellen Miller</i>
			10. PM TEAM NUMBER <i>12</i>

14. CHECK IF APPLICABLE <input type="checkbox"/> Public Health/Quarantine <input type="checkbox"/> Minor Use <input type="checkbox"/> Substitute Chemical <input type="checkbox"/> Part of IPM <input type="checkbox"/> Seasonal Concern <input type="checkbox"/> Review Requires Less Than 4 Hours	<i>AH</i>
	TO BE COMPLETED BY PCB
	11. DATE SENT TO HED/TSS <i>02-04-86</i>
	12. PRIORITY NUMBER <i>49</i>
	13. PROJECTED RETURN DATE <i>05-23-86</i>

15. INSTRUCTIONS TO REVIEWER A. HED <input type="checkbox"/> Total Assessment - 3(c)(5) <input type="checkbox"/> Incremental Risk Assessment - 3(c)(7) and/or E.L. Johnson memo of May 12, 1977. B. SPRD (Send Copy of Form to SPRD PM) <input type="checkbox"/> Chemical Undergoing Active RPAR Review <input type="checkbox"/> Chemical Undergoing Active Registration Standards Review C. <input type="checkbox"/> BFSD D. <input type="checkbox"/> TSS/RD E. <input type="checkbox"/> Other	F. INSTRUCTIONS <i>161-1 - Hydrolysis Date - Reregistration</i>
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16. RELATED ACTIONS

17. 3(c)(1)(D) <input type="checkbox"/> Use Any or All Available Information <input type="checkbox"/> Use Only Attached Data <input type="checkbox"/> Use Only the Attached Data for Formulation and Any or All Available Information on the Technical or Manufacturing Chemical.	18. REVIEWS SENT TO <input type="checkbox"/> TB <input type="checkbox"/> EEB <input type="checkbox"/> EF <input type="checkbox"/> PL <input type="checkbox"/> RCB <input type="checkbox"/> EFB <input type="checkbox"/> CH <input type="checkbox"/> BFSD
---	--

19.	To	TYPE OF REVIEW	NUMBER OF ACTIONS							
			Registration	Petition	EUP	SLN	Sec. 18	Inert	MNR. USE	Other
HED		TOXICOLOGY								
		ECOLOGICAL EFFECTS								
		RESIDUE CHEMISTRY								
	<input checked="" type="checkbox"/>	ENVIRONMENTAL DATA <i>2-4-86 1</i>								
RD/TSS		CHEMISTRY								
		EFFICACY								
		PRECAUTIONARY LABELING								
BFSD		ECONOMIC ANALYSIS								

20. <input type="checkbox"/> Label Submitted with Application Attached	21. <input type="checkbox"/> Confidential Statement of Formula	22. <input type="checkbox"/> Representative Labels Showing Accepted Uses Attached	23. Date Returned to RD (to be completed by HED)	24. Include an Original and 4 (four) Copies of This Completed Form for Each Branch Checked for Review.
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CONFIDENTIAL DATA

SOME INFORMATION IN THE ATTACHED MATERIAL IS ENTITLED TO TREATMENT AS TRADE SECRET OR PROPRIETARY DATA UNDER SECTION 7(D) AND SECTION 10 OF PL 92-516 AS AMENDED BY PL 94-140.

ANY PERSON HANDLING OR USING THE ATTACHED DATA IN ANY WAY IS RESPONSIBLE FOR PREVENTING UNAUTHORIZED DISCLOSURE WHILE IN HIS POSSESSION. SECTION 14(b)(3) OF FIRRA PROVIDES FOR A PENALTY OF UP TO \$10,000 FINE AND UP TO 3 YEARS IMPRISONMENT FOR UNAUTHORIZED DISCLOSURE INVOLVING INTENT TO DEFRAUD.

THE ATTACHED INFORMATION IS NOT TO BE PUBLISHED, PUBLICLY DISCUSSED, INCLUDED IN RESPONSE TO AN FOI REQUEST OR OTHERWISE RELEASED WITHOUT THE EXPLICIT, WRITTEN AUTHORIZATION OF THE APPROPRIATE DIVISION DIRECTOR (WITHIN THE OFFICE OF PESTICIDE PROGRAMS, OFFICE OF TOXIC SUBSTANCES, ENVIRONMENTAL PROTECTION AGENCY).

CONFIDENTIAL DATA

1. CHEMICAL: Common name:

Chlorpyrifos

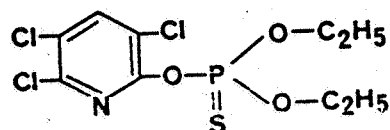
Chemical name:

O,O-Diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate

Trade name(s):

CHLORPYRIFOS, BRODAN, DOWCO, DURSBAN, ERADEX, LORSBAN,
PYRINEX

Structure:



Formulations:

0.1-25% D, 0.075-15% G, 1% P/T, 2.32-50% WP, 10.6% Mcap,
0.5-10% Impr, 0.15625-4 lb/gal and 0.51-41.2% EC,
6 lb/gal SC/L, 0.073125-3.8 lb/gal and 0.05-0.86% RTU,
0.09-0.5% PrL

Physical/Chemical properties:

Molecular formula: $C_9H_{11}Cl_3NO_3PS$

Molecular weight: 34250.57

Physical state: White granular crystal

Melting Point: 41.5-43.5°C

Vapor Pressure: 4.22×10^{-5}

Solubility: Water: 2 ppm at 25°C.

Organic solvents (% of solution at 25°C):

Isooctane 79%

Methanol 43%

Readily soluble in other organic solvents

2. TEST MATERIAL:

See individual studies.

3. STUDY/ACTION TYPE:

Addendum to the Chlorpyrifos Registration Standard.

4. STUDY IDENTIFICATION:

The following studies have been reviewed:

McCall, P.J. 1985a. Chlorpyrifos aged column leaching study. Report GH-C 1778. Submitted by Dow Chemical U.S.A, Agricultural Products Department, Midland, MI. Acc. No. 260794. Reference 3.

McCall, P.J. 1985b. Column leaching and sorption studies with chlorpyrifos. Report GH-C 1777. Submitted by Dow Chemical U.S.A., Agricultural Products Department, Midland, MI. Acc. No. 260794. Reference 2.

McCall, P.J. 1986. Hydrolysis of chlorpyrifos in dilute aqueous solution. Report GH-C 1791. Submitted by Dow Chemical U.S.A., Agricultural Products Department, Midland, MI. Acc. No. 260794. Reference 1.

McCall, P.J., R.L. Swann, and W.R. Bauriedel. 1985. Volatility characteristics of chlorpyrifos from soil and corn. Submitted by Dow Chemical Co., Midland, MI. Acc. No. 260794. Reference 4.

The following study was not reviewed because it contains exposure data only:

Bohl, R.W. and G. Huitink. 1985. Potential exposure monitoring for chlorpyrifos in a mature cornfield following aerial spraying of four different carrier formulations of Lorsban 4E, Saunders County, Nebraska, July 24-27, 1984. Submitted by Dow Chemical U.S.A., Midland, MI. Acc. No. 260794. References 5 and 6.

5. REVIEWED BY:

Hudson Boyd
Chemist
EAB/HED/OPP

Signature: Hudson Boyd

Date: 10-23-86

6. APPROVED BY:

Emil Regelman
Supervisory Chemist
Review Section #3, EAB/HED/OPP

Signature: Emil Regelman

Date: OCT 25 1986

7. CONCLUSIONS

7.1 Hydrolysis (161-1)

The study by McCall (1986) was valid and fulfilled EPA Guidelines requirements for hydrolysis testing.

Under environmental conditions (pH 5-7 and 25°C) chlorpyrifos hydrolyzes slowly and the hydrolytic half-life is approximately 72 days. In an alkaline environment (pH 9) hydrolysis proceeds more rapidly and the half-life is approximately 16 days.

Two degrades, viz, 3,5,6-trichloro-2-pyridinol and O-ethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate are the products of hydrolysis. ←

7.2 Mobility - Leaching/Adsorption/Desorption (163-1)

The studies by McCall (1985 a,b) were valid but provided only part of the data required by Sec 163-1 of Subdivision N (Pesticide Assessment Guidelines). A study is still needed on the desorption of chlorpyrifos from the four soils or on the leaching of unaged chlorpyrifos through one additional soil and one sediment.

Chlorpyrifos is slightly mobile to mobile in sandy loam and silt loam; the adsorption and leaching of the chemical is positively influenced by the organic carbon content of the soil - most of the applied chlorpyrifos will remain in the upper two inches of soil having an organic carbon content above 1%. Consequently, chlorpyrifos would not appear to be a potential groundwater contaminant in sandy loam or loam soils. ←

7.3 Metabolism-aerobic soil (162-1)

The study by McCall (1985 b) is valid and completes EPA data requirements for aerobic soil metabolism, partially fulfilled by earlier studies.

The half-life of chlorpyrifos in aerobic soils under environmental conditions is expected to be about 7-10 days. A major degradate would be 3,5,6-trichloro-2-pyridinol.

7.4 Volatility (Laboratory study) (163-2)

Although the study of McCall, et al, (1985) investigating volatilization from plants was valid and provided useful information it failed to provide data on air concentrations in units per volume or units per time.

The work on volatility from soil could not be validated because of an inadequate testing/data gathering procedure. Consequently this study does not fulfill EPA Guideline requirements for volatility testing.

8. RECOMMENDATIONS:

8.1 Accept the data developed by McCall (1986) on the hydrolysis of chlorpyrifos as fulfilling the EPA requirements of Subdivision N, Sec. 161-1.

8.2 Require the registrant to provide additional data on leaching/adsorption/desorption (163-1) of chlorpyrifos as follows:

- ° Either desorption from the four soils on which adsorption data were obtained, or
- ° Leaching of unaged chlorpyrifos through one additional soil and one sediment.

- 8.3 Accept the data developed by McCall (1985b) on the aerobic soil metabolism of chlorpyrifos as fulfilling EPA requirements of Subdivision N, Sec. 162-1.
- 8.4 Require the registrant to state the volatilization of chlorpyrifos from plants in units per volume or in units per time.

Require repetition of the study on volatilization from soil to confirm the application rate and the efficiency of the trapping media.

Require the registrant to provide data on the vapor pressure and the water solubility of chlorpyrifos.

If possible, material balances at each sampling interval should be given.

9. BACKGROUND:

A. Introduction

Chlorpyrifos has been previously reviewed by Dynamac for the Standard and one addendum.

B. Description of the Chemical and of its Use:

Chlorpyrifos is a broad spectrum insecticide which is active by contact, ingestion, and vapor action. It is registered for use on tree fruit and nut crops; field and vegetable crops; ornamentals (including greenhouses); lawns and ornamental turf; domestic outdoor and indoor sites; commercial establishments (edible and nonedible product areas); aquatic noncrop sites; terrestrial noncrop sites; poultry, pet, and animal housing; and on beef cattle and dogs. Chlorpyrifos is also used as a seed treatment.

An estimated 7.0-11.0 million pounds of active ingredient are produced each year in the United States for domestic use. Of the total domestic chlorpyrifos usage, 57% is applied to corn and 5-6% to cotton. Commercial pest control and lawn and garden services use 20-22% of annual chlorpyrifos consumption followed by domestic household and lawn and garden use (9-13%). Application rates range from 0.1 oz/A for some seed treatments to \approx 50 lb/A for certain tree fruit applications.

Chlorpyrifos may be formulated with allethrin, d-trans-allethrin, s-bioallethrin, fenfluralin, bis(tributyltin)oxide, chlorthal-methyl, copper 8-quindinolate, diazinon, dichlorvos, diplenamid, methyl parathion, monuron, N-octyl bicycloheptene dicarboximide, phenothrin, piperonyl butoxide, pyrethrins, resmethrin, siduron, Sulfox-cide, tetramethrin, thiophanate-methyl, and toxaphene.

Single active ingredient formulations of chlorpyrifos consist of 0.1-25% D, 0.075-15% G, 1% P/T, 2.32-50% WP, 10.6% Mcap, 0.5-10% Impr, 0.15625-4 lb/gal and 0.51-41.2% EC, 6 lb/gal SC/L, 0.073125-3.8 lb/gal and 0.05-0.86% RTU, and 0.09-0.5% PrL. The D formulations are applied as seed treatments and as spot treatments in domestic dwellings. The G formulations are banded or broadcast with ground equipment or aerially and can be used as spot treatments in and around animal quarters and domestic dwellings. The WP is used as a seed treatment and is also applied as a spray to turkey pens. The Impr formulations are placed as baits or as impregnated strips. The EC formulations are applied as sprays with ground equipment or aerially; as dips or sprays for cattle and nursing stock; sprayed or painted on animal quarters or domestic dwellings; or by trenching, rodding, injection or low pressure sprays around terrestrial structures. RTU formulations are also painted or sprayed around animal quarters and domestic dwellings and as a spot treatment on cattle. The SC/L is applied exclusively as a fog for mosquito control. The P/T formulation may be applied by aircraft. PrL formulations are applied as sprays to dogs and in and around animal quarters and domestic dwellings. Indoor use of chlorpyrifos formulations above 0.5% is limited to professional pest control operators. Chlorpyrifos can be applied for mosquito control only by or under supervision of public health organizations, mosquito abatement districts, or other trained personnel responsible for insect control programs.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

See attached reviews of individual studies.

11. COMPLETION OF ONE-LINER:

One liner amended.

12. CBI APPENDIX:

All data reviewed here are considered CBI by the registrant and must be treated as such.

DYNAMAC
CORPORATION

CHLORPYRIFOS ADDENDUM II

Final Report

**Task 1: Review and Evaluation of
Individual Studies**

**Task 2: Environmental Fate and
Exposure Assessment**

Contract No. 68-02-4250

OCTOBER 8, 1986

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852

CHLORPYRIFOS

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INTRODUCTION

Chlorpyrifos is a broad spectrum insecticide which is active by contact, ingestion, and vapor action. It is registered for use on tree fruit and nut crops; field and vegetable crops; ornamentals (including greenhouses); lawns and ornamental turf; domestic outdoor and indoor sites; commercial establishments (edible and nonedible product areas); aquatic noncrop sites; terrestrial noncrop sites; poultry, pet, and animal housing; and on beef cattle and dogs. Chlorpyrifos is also used as a seed treatment.

An estimated 7.0-11.0 million pounds of active ingredient are produced each year in the United States for domestic use. Of the total domestic chlorpyrifos usage, 57% is applied to corn and 5-6% to cotton. Commercial pest control and lawn and garden services use 20-22% of annual chlorpyrifos consumption followed by domestic household and lawn and garden use (9-13%). Application rates range from 0.1 oz/A for some seed treatments to ~50 lb/A for certain tree fruit applications.

Chlorpyrifos may be formulated with allethrin, d-trans-allethrin, s-bioallethrin, fenfluralin, bis(tributyltin)oxide, chlorthal-methyl, copper 8-quindinolate, diazinon, dichlorvos, diplenamid, methyl parathion, monuron, N-octyl bicycloheptene dicarboximide, phenothrin, piperonyl butoxide, pyrethrins, resmethrin, siduron, Sulfox-cide, tetramethrin, thiophanate-methyl, and toxaphene.

Single active ingredient formulations of chlorpyrifos consist of 0.1-25% D, 0.075-15% G, 1% P/T, 2.32-50% WP, 10.6% Mcap, 0.5-10% Impr, 0.15625-4 lb/gal and 0.51-41.2% EC, 6 lb/gal SC/L, 0.073125-3.8 lb/gal and 0.05-0.86% RTU, and 0.09-0.5% PrL. The D formulations are applied as seed treatments and as spot treatments in domestic dwellings. The G formulations are banded or broadcast with ground equipment or aerially and can be used as spot treatments in and around animal quarters and domestic dwellings. The WP is used as a seed treatment and is also applied as a spray to turkey pens. The Impr formulations are placed as baits or as impregnated strips. The EC formulations are applied as sprays with ground equipment or aerially; as dips or sprays for cattle and nursing stock; sprayed or painted on animal quarters or domestic dwellings; or by trenching, rodding, injection or low pressure sprays around terrestrial structures. RTU formulations are also painted or sprayed around animal quarters and domestic dwellings and as a spot treatment on cattle. The SC/L is applied exclusively as a fog for mosquito control. The P/T formulation may be applied by aircraft. PrL formulations are applied as sprays to dogs and in and around animal quarters and domestic dwellings. Indoor use of chlorpyrifos formulations above 0.5% is limited to professional pest control operators. Chlorpyrifos can be applied for mosquito control only by or under supervision of public health organizations, mosquito abatement districts, or other trained personnel responsible for insect control programs.

CASE GS0100 CHLORPYRIFOS STUDY 1 PM --

CHEM 059101 Chlopyrifos

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 02
McCall, P.J. 1986. Hydrolysis of chlorpyrifos in dilute aqueous solution.
Report GH-C 1791. Submitted by Dow Chemical U.S.A., Agricultural Products
Department, Midland, MI. Acc. No. 260794. Reference 1.-----
SUBST. CLASS = S.-----
DIRECT RVW TIME = 4 1/2 (MH) START-DATE END DATE-----
REVIEWED BY: P. Perreault
 TITLE: Staff Scientist
 ORG: Dynamac Corp., Rockville, MD
 TEL: 468-2500-----
APPROVED BY: H. Boyd
 TITLE: Chemist
 ORG: EAB/HED/OPP
 TEL: 557-7463

SIGNATURE:

DATE:

CONCLUSIONS:Degradation - Hydrolysis

1. This study is scientifically valid.
2. 2,6-Pyridine ring-labeled [¹⁴C]chlorpyrifos (purity 97.9%), at ~0.6 ppm, degraded with calculated half-lives of 72.8 days at pH 5, 72.1 days at pH 7, and 15.8 days at pH 9 in sterile buffered solutions incubated in the dark at 25°C for 35 days. Two degradates were formed and were identified as 3,5,6-trichloro-2-pyridinol and O-ethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate.
3. This study fulfill's EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of chlorpyrifos at pH 5, 7, and 9.

MATERIALS AND METHODS:

2,6-Pyridine ring-labeled [¹⁴C]chlorpyrifos (radiochemical purity 97.9%, specific activity 14.2 mCi/mmol, Dow Chemical U.S.A) in acetone was added at ~0.6 ppm to capped centrifuge tubes containing samples (50 ml) of sterile city water adjusted to pH 5, 7, and 9 at 0.005 M with phos-

phate buffers. The solutions were incubated in the dark at 25°C and were sampled at various intervals up to 35 days after treatment.

Aliquots (1.1 ml) of the solutions were divided into two parts for analysis. One part (0.1 ml) was analyzed for total radioactivity using LSC. The LSC counting efficiencies ranged from 78.7 to 103.8%. The remaining aliquot (1.0 ml) was analyzed for chlorpyrifos and its degradates by HPLC. Degradates were characterized by injecting the remaining hydrolysis solutions on the HPLC column and then collecting and pooling the fractions containing the individual radioactive peaks for analysis. The peaks were coinjected with analytical standards using two different sets of gradient elution conditions, under which the columns were eluted with water and methanol buffered with either 0.01 M ammonium acetate (Condition A) or 1.0% acetic acid (Condition B). The pooled fractions were acidified with 0.1 N hydrochloric acid and extracted three times with diethyl ether. The ether extracts were pooled, dried over sodium sulfate, and concentrated. The concentrated fractions were then reacted with either N,O-bis-(trimethylsilyl) acetamide or diazomethane and analyzed by GC/MS.

REPORTED RESULTS:

[¹⁴C]Chlorpyrifos, at ~0.6 ppm in sterile buffered water incubated at 25°C, degraded with calculated half-lives of 72.8 days at pH 5, 72.1 days at pH 7, and 15.8 days at pH 9 (Figures 1-3). Two degradates were formed and were identified as 3,5,6-trichloro-2-pyridinol and O-ethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate (Table 1).

DISCUSSION:

1. Method detection limits were not reported.
2. After one week, the data at pH 9 showed a decrease in the rate of hydrolysis resulting from a change in pH in these samples to a value of ~8.0. The change in pH was attributed to the production of O,O-diethyl phosphorothioic acid. In order to obtain an accurate estimate of the hydrolysis rate at pH 9, the first order plot included only data from the first four time points (Figure 3).

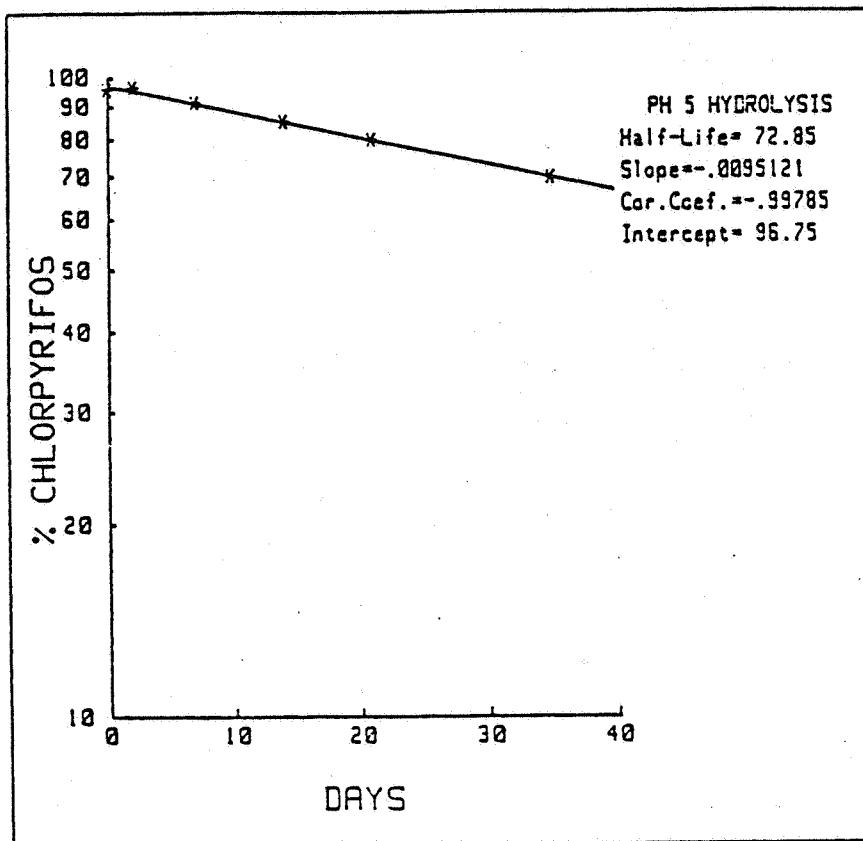


Figure 1. Chlorpyrifos degradation in sterile solution buffered at pH 5 and incubated in the dark at 25°C.

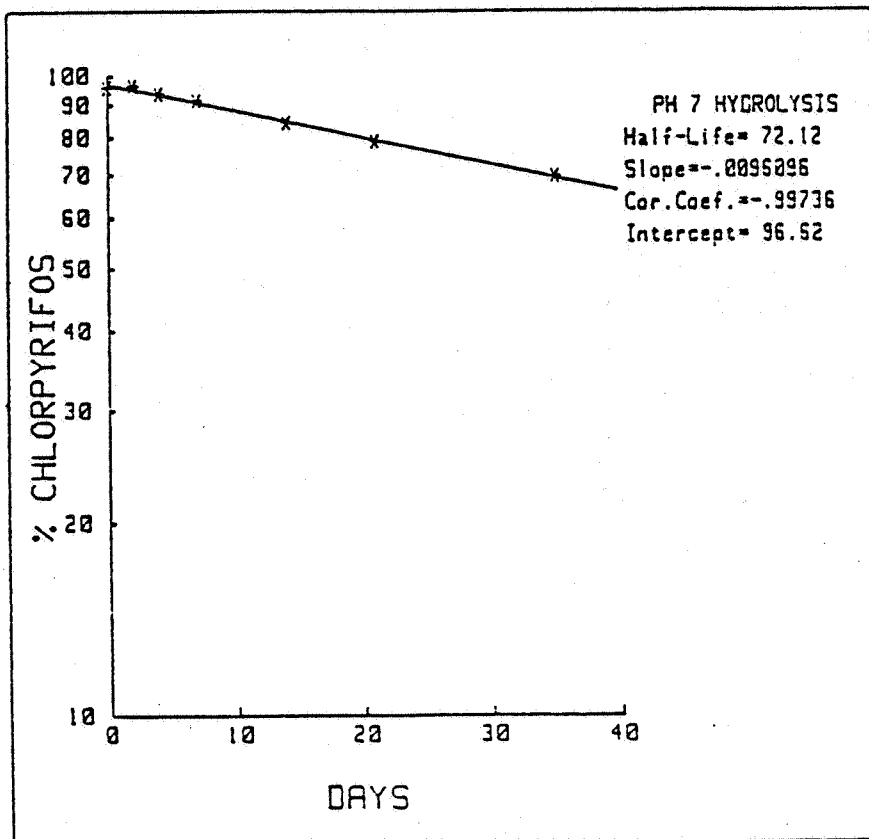


Figure 2. Chlorpyrifos degradation in sterile solution buffered at pH 7 and incubated in the dark at 25°C.

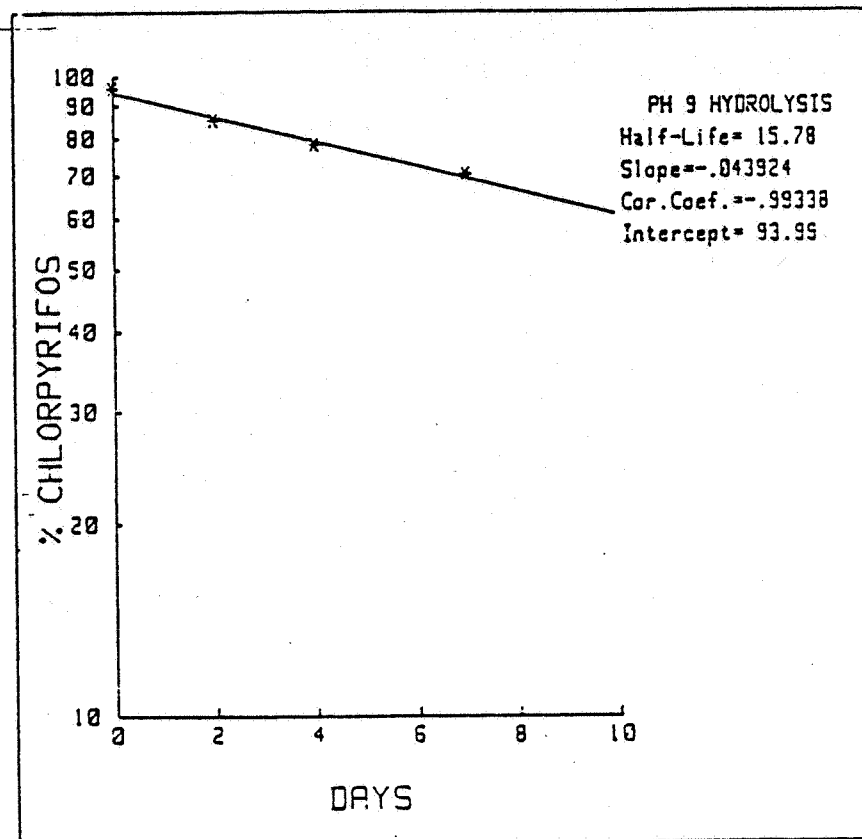


Figure 3. Chlorpyrifos degradation in sterile solution buffered at pH 9 and incubated in the dark at 25°C.^a

^a Includes data for the first seven days of the study only.

Table 1. [¹⁴C]Chlorpyrifos and its degradates (% of applied) in buffered solutions treated with [¹⁴C]chlorpyrifos at ~0.6 ppm and incubated in the dark at 25°C.

Sampling interval (days)	Chlorpyrifos	3,5,6-Trichloro-2-pyridinol	O-Ethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioic acid
<u>pH 5</u>			
0.0	95.4	4.6	ND ^a
2.0	96.0	4.0	ND
7.0	90.8	5.9	3.3
14.0	84.8	7.5	7.7
21.0	79.3	9.6	11.1
35.0	69.2	13.2	17.7
<u>pH 7</u>			
0.0	95.4	4.6	ND
2.0	96.0	4.0	ND
4.0	93.2	5.0	1.8
7.0	90.9	5.8	3.3
14.0	83.9	8.5	7.6
21.0	78.5	10.9	10.6
35.0	69.3	14.3	16.4
<u>pH 9^b</u>			
0.0	95.4	4.6	ND
2.0	85.0	12.9	1.5
4.0	77.8	19.0	1.8
7.0	69.9	27.0	3.1
14.0	57.5	36.8	5.7
21.0	54.5	37.8	7.7
35.0	39.6	47.9	12.5

^a Not detected; detection limit not reported.

^b After week 4, pH declined from 9.0 to ~8.0.

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CASE GS0100 CHLORPYRIFOS STUDY 2 PM --

CHEM 059101 Chlopyrifos

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 02
McCall, P.J. 1985b. Column leaching and sorption studies with chlorpyrifos.
Report GH-C 1777. Submitted by Dow Chemical U.S.A., Agricultural Products
Department, Midland, MI. Acc. No. 260794. Reference 2.-----
SUBST. CLASS = S.-----
DIRECT RVW TIME = 5 (MH) START-DATE END DATE-----
REVIEWED BY: P. Perreault
TITLE: Staff Scientist
ORG: Dynamac Corp., Rockville, MD
TEL: 468-2500-----
APPROVED BY: H. Boyd
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-7463

SIGNATURE:

DATE:

CONCLUSIONS:Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. [¹⁴C]Chlorpyrifos (purity >98%) was slightly mobile to mobile in sandy loam, loam, and silt loam soils, based on batch equilibrium and column leaching studies. The adsorption and leaching of [¹⁴C]chlorpyrifos were positively affected by the organic carbon content of the soil. Adsorption coefficients (K_d) ranged from 49.9 in a loam soil (organic carbon content 0.68%) to 99.7 in a silt loam soil (organic carbon content 2.01%). In soil columns, ~5% of the applied chlorpyrifos leached below the upper 5 cm in the loam soil, while <1% of the applied chlorpyrifos leached below the upper 5 cm of the sandy loam and silt loam soils (the two soils highest in organic carbon).
3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility of unaged chlorpyrifos in columns of three soils and on the adsorption of chlorpyrifos in three soils.

MATERIALS AND METHODS:

Experiment 1

2,6-Pyridine ring-labeled [^{14}C]chlorpyrifos (radiochemical purity >98%, specific activity 1.99 mCi/mmol, Dow Chemical U.S.A.) in acetone was added at 1 ppm to a slurry consisting of 4 g of sieved (2 mm) soil and 15 ml of a 0.1 N calcium sulfate solution (Table 1). The mixture was shaken overnight, then centrifuged for 1 hour and the supernatant removed. Aliquots of the supernatant were analyzed for total radioactivity using LSC and for chlorpyrifos using HPLC.

Experiment 2

Columns (30-cm depth, 17-mm width) of the same soils were saturated with the calcium sulfate solution. [^{14}C]Chlorpyrifos was applied to the surface of the columns at 0.5 kg ai/ha. The columns were eluted with 20 inches of the calcium sulfate solution at a flow rate of ~1 ml/hour. Following leaching, the columns were frozen and cut into 1-cm segments. Each segment was extracted with acetone, and the extracts were analyzed for total radioactivity using LSC.

REPORTED RESULTS:

Experiment 1

Sorption coefficients (K_d) ranged from 49.9 for the loam soil to 99.7 for the silt loam soil, indicating a correlation between organic matter content and chlorpyrifos adsorption (Table 2).

Experiment 2

In the soil columns, >95% of the chlorpyrifos residues remained in the top 2 cm of soil for all three soil types (Table 3). In the sandy loam and silt loam soils (the two soils highest in organic carbon), <1% of the applied radioactivity was found below the upper 5 cm of the soil columns, while the loam soil had ~5% of the applied below the upper 5 cm.

DISCUSSION (both experiments):

1. The CEC of the soils was not reported.
2. In the batch equilibrium portion of the study, desorption of chlorpyrifos was not studied. Experimental procedures and protocols were adequate to assess chlorpyrifos adsorption on soil.
3. Based on the results of Experiment 1 (batch equilibrium portion of the study) chlorpyrifos would be classified as moderately mobile; however, the results from Experiment 2 (column leaching portion of the study) would classify chlorpyrifos as a low mobility pesticide in all three soils.

Table 1. Soil characteristics.

Soil type	Source	Sand	Silt	Clay	Organic carbon	pH
		%				
Commerce loam	Mississippi	38	48	14	0.68	6.7
Tracy sandy loam	Indiana	56	30	14	1.12	6.2
Catlin silt loam	Illinois	12	56	32	2.01	6.2

Table 2. Adsorption coefficients for batch equilibrium studies and leaching distances in soil columns eluted with 20 inches of 0.1 N calcium ion solution for [¹⁴C]chlorpyrifos residues.

Soil type ^a	Sorption coefficients ^b		Leaching distance ^c (cm)
	K _d	K _{oc}	
Commerce loam	49.9	7300	1
Tracy sandy loam	65.6	5860	1
Catlin silt loam	99.7	4960	1

^a Soil characteristics presented in Table 1.

^b K_d = chlorpyrifos bound to soil/chlorpyrifos in supernatant.
K_{oc} = chlorpyrifos per gram of organic carbon/chlorpyrifos per gram of supernatant.

^c Point of maximum concentration of chlorpyrifos in the soil column.

Table 3. Distribution of radioactivity (% of applied) in three soil columns treated with unaged [¹⁴C]chlorpyrifos and leached with 20 inches of water.

Sampling depth (cm)	Commerce loam	Tracy sandy loam	Catlin silt loam
0-1	89.7	79.1	95.8
1-2	5.2	18.4	2.8
2-3	0.3	0.9	0.6
3-4	0.2	0.3	0.2
4-5	0.2	0.4	0.1
5-6	0.2	0.3	0.1
6-7	0.2	0.1	<0.1
7-8	0.2	0.2	<0.1
9-10	0.2	0.1	<0.1
10-11	0.2	0.1	<0.1
11-12	0.2	<0.1	<0.1
12-13	0.2	<0.1	<0.1
13-14	0.1	<0.1	<0.1
14-15	0.2	<0.1	<0.1
15-16	0.2	<0.1	<0.1
16-17	0.2	<0.1	<0.1
17-18	0.1	<0.1	<0.1
18-19	0.2	<0.1	<0.1
19-20	0.1	<0.1	<0.1
20-21	0.2	<0.1	<0.1
21-22	0.2	<0.1	<0.1
22-23	0.1	<0.1	<0.1
23-24	0.2	<0.1	<0.1
24-25	0.2	<0.1	<0.1
Radioactivity in soil columns	99.2	>99.9	>99.6
Radioactivity in leachate	1.3	0.3	0.3
Total	100.5	>100.2	>99.9

CASE GS0100 CHLORPYRIFOS STUDY 3 PM --

CHEM 059101 Chlopyrifos

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 02
McCall, P.J. 1985a. Chlorpyrifos aged column leaching study. Report GH-C
1778. Submitted by Dow Chemical U.S.A, Agricultural Products Department,
Midland, MI. Acc. No. 260794. Reference 3.-----
SUBST. CLASS = S.-----
DIRECT RVW TIME = 6 (MH) START-DATE END DATE-----
REVIEWED BY: P. Perreault
 TITLE: Staff Scientist
 ORG: Dynamac Corp., Rockville, MD
 TEL: 468-2500-----
APPROVED BY: H. Boyd
 TITLE: Chemist
 ORG: EAB/HED/OPP
 TEL: 557-7463

SIGNATURE:

DATE:

CONCLUSIONS:Metabolism - Aerobic Soil

1. This study is scientifically valid.
2. 2,6-Pyridine ring-labeled [¹⁴C]chlorpyrifos (purity 97.9%), at 1.2 ppm, in a sandy loam soil maintained under aerobic conditions at 25°C in the dark, degraded with a half-life of 7-10 days. One major degradate, identified as 3,5,6-trichloro-2-pyridinol, was formed (maximum 28.1% at 10 days posttreatment). ←
3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the degradation of chlorpyrifos in an aerobic soil.

Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. Aged (10 days) 2,6-pyridine ring-labeled [¹⁴C]chlorpyrifos (purity 97.9%) residues were moderately mobile in a sandy loam soil after leaching with

20 inches of water; 73% of the applied remained in the upper 5 cm of the column. The remaining [¹⁴C]residues were distributed fairly evenly throughout the column and in the column leachate. Chlorpyrifos and 3,5,6-trichloro-2-pyridinol were the major components of the residues. 3,5,6-Trichloro-2-pyridinol (purity 99%) had adsorption coefficients (K_d) of 0.37 and 0.33 in two different samples of the sandy loam soil.

3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility of aged chlorpyrifos residues in soil.

MATERIALS AND METHODS:

Metabolism - Aerobic Soil

Londo sandy loam soil (68% sand, 20% silt, 12% clay, 1.9% organic carbon, pH 7.5) was sieved (2 mm), placed in one compartment of a two-compartment incubation flask, and treated with 2,6-pyridine ring-labeled [¹⁴C]chlorpyrifos (radiochemical purity 97.9%, 14.2 mCi/mmol, Dow Chemical U.S.A) in acetone at 1.2 ppm. The second compartment of the flask contained 0.2 N NaOH as a CO₂ trap. The flasks were aged under aerobic conditions at 25°C in the dark for 0, 7, 10, or 35 days. Following the aging period, total radioactivity in each sample flask was determined by analysis of the NaOH for volatilized ¹⁴CO₂ using LSC and by analysis of the soil for nonvolatilized radioactivity using combustion and LSC. Soil samples were then extracted once with phosphoric acid and diethyl ether and three additional times with ether. The extracts were partitioned and aliquots of the ether and acid fractions were analyzed for total radioactivity using LSC. Total radioactivity in samples of extracted soil was determined by LSC following combustion. The ether extracts were then analyzed for chlorpyrifos and its degradates using HPLC.

Mobility - Leaching and Adsorption/Desorption

Experiment 1

A layer (2 cm) of the aged (10 days) Londo sandy loam soil was added to the top of soil columns (40-cm depth, 22-mm width) filled with air-dried untreated Londo sandy loam soil (30-cm depth). The columns were saturated from the bottom and then eluted with 20 inches of water at a flow rate of 0.5 ml/minute. Following leaching, the columns were frozen and cut into 5-cm segments. Each segment was thoroughly mixed and analyzed for total radioactivity using combustion and LSC. Samples of each segment of soil were extracted with phosphoric acid and diethyl ether. The extracts were analyzed for chlorpyrifos and its degradates using HPLC. Total radioactivity in the leachate was determined by using LSC. Aliquots of the leachate were then acidified with 1.0 N HCl, extracted three times with ether, and total radioactivity in the ether extracts was determined by LSC. The ether extracts were dried with sodium sulfate, concentrated, and degradates were characterized using HPLC.

Experiment 2

To determine the sorption properties of the major degradate, 2,6-ring-labeled [¹⁴C]3,5,6-trichloro-2-pyridinol (radiochemical purity 99%, specific activity 1.98 mCi/mmol, source unspecified) in an aqueous solution was added at ~1.2 ppm to Londo sandy loam soil in centrifuge tubes. The tubes were shaken for 4 hours and centrifuged for 30 minutes to separate the soil from the water. The aqueous fraction was then analyzed for total radioactivity using LSC.

REPORTED RESULTS:

Metabolism - Aerobic Soil

[¹⁴C]Chlorpyrifos, at 1.2 ppm in Londo sandy loam soil, degraded with a half-life of 7-10 days under the conditions of this study (Figure 1). One major degradate, identified as 3,5,6-trichloro-2-pyridinol, was formed and reached a peak concentration at 10 days (Table 1).

Mobility - Leaching and Adsorption/Desorption

Experiment 1

In soil columns, the majority (73.1%) of aged [¹⁴C]chlorpyrifos residues remained in the top 5 cm of soil. The remaining [¹⁴C]residues were distributed fairly uniformly throughout the column and in the column leachate. The major degradate, 3,5,6-trichloro-2-pyridinol, was found distributed throughout the column and accounted for all of the radioactivity recovered from the leachate (Table 2).

Experiment 2

Sorption coefficients (K_d) were 0.37 and 0.33 for two different samples of the treated sandy loam soil, indicating that 3,5,6-trichloro-2-pyridinol was moderately mobile under the conditions of the experiment.

DISCUSSION:

General (both studies)

1. The test soil was not completely characterized; the CEC of the soil was not reported.
2. Method detection limits were not reported.

Metabolism - Aerobic Soil

Recovery values, based on combustion data and analysis of the NaOH, were low (80-90%). However, overall recovery, based on the sum of [¹⁴C]residues in the NaOH, the diethyl ether extract, the acid extract, and the combustion of extracted soil, was adequate (92-97%).

Mobility - Leaching and Adsorption/Desorption

Experiment 1

K_d values were not reported.

Experiment 2

1. It was not specified whether or not the experiment was conducted in a 0.01 N calcium ion solution.
2. The temperature at which the study was conducted was not specified.
3. Desorption of the test substance was not studied.
4. Adsorption was studied on only one type of soil; however, the one soil type used (sandy loam soil) was adequate for the purposes of this experiment.

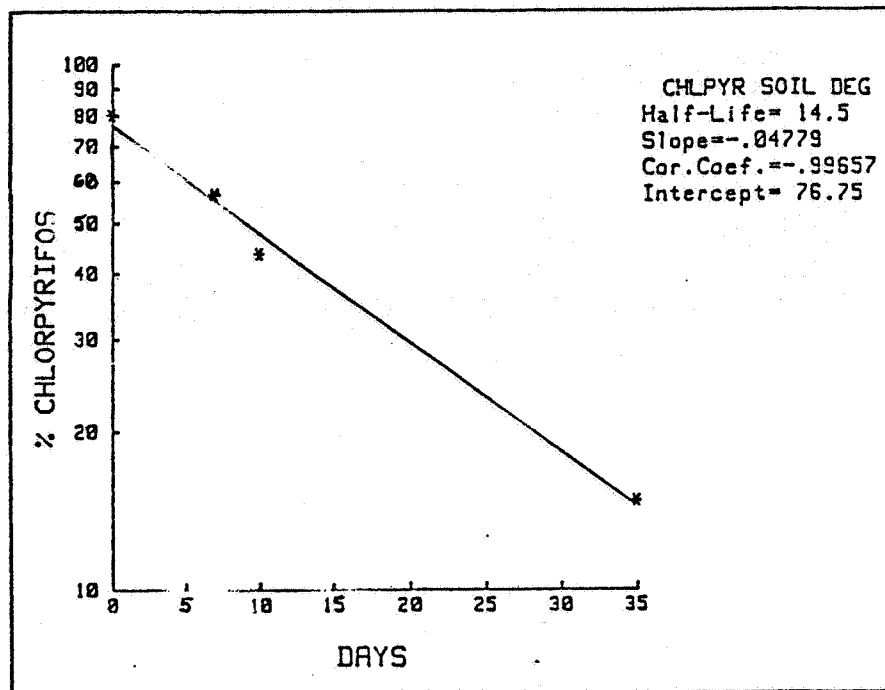


Figure 1. Degradation of [¹⁴C]chlorpyrifos in Londo sandy loam soil treated with [¹⁴C]chlorpyrifos at 1.2 ppm and maintained under aerobic conditions at 25°C in the dark.

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Table 1. [¹⁴C]Chlorpyrifos and its degradates (% of applied) in Londo sandy loam soil treated with [¹⁴C]chlorpyrifos at 1.2 ppm and maintained under aerobic conditions at 25°C in the dark.

Sampling interval (days)	Chlorpyrifos ^a	3,5,6-Trichloro-2-pyridinol ^a	Other ^a	[¹⁴ C]residues in phosphoric acid extracts	Non-extractable	¹⁴ C ₀₂	Total [¹⁴ C]
0	80.2	0.8	1.0	0.15	11.0	0.0	93.15
7	56.5	22.8	0.4	0.22	10.2	2.8	92.92
10	43.5	28.1	2.0	0.40	15.2	4.5	93.70
35	14.7	26.6	2.7	5.40	14.8	31.6	95.80

^a Percent of applied [¹⁴C]residues found in diethyl ether soil extract.

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Table 2. Distribution of total [¹⁴C]residues (% of applied) in soil columns filled with sandy loam soil treated with aged (10 days) [¹⁴C]chlorpyrifos, at 1.2 ppm, and leached with 20 inches of water.

Sampling depth (cm)	Chlorpyrifos	Pyridinol	Non-extractable	Total [¹⁴ C]
0-5	48.7	11.1	11.6	73.1
5-10	0.1	2.1	0.1	3.0
10-15	0.0	3.3	0.1	3.7
15-20	0.0	4.1	0.1	4.9
20-25	0.0	5.4	0.1	5.4
25-30	0.0	5.4	0.1	3.6
Radioactivity in soil columns	48.8	31.4	12.1	93.7
Radioactivity in leachate ^a	0.0	4.7	1.5	6.2
Total	48.8	36.1	13.6	99.9

^a Total volume was 192 ml.

CASE GS0100 CHLORPYRIFOS STUDY 4 PM --

 CHEM 059101 Chlopyrifos

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT AND 12 - EMULSIFIABLE CONCENTRATE (EC)

 FICHE/MASTER ID No MRID CONTENT CAT 02
 McCall, P.J., R.L. Swann, and W.R. Bauriedel. 1985. Volatility characteristics of chlorpyrifos from soil and corn. Submitted by Dow Chemical Co., Midland, MI. Acc. No. 260794. Reference 4.

 SUBST. CLASS = S.

 DIRECT RVW TIME = 5 (MH) START-DATE END DATE

 REVIEWED BY: L. Binari
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SIGNATURE:

DATE:

CONCLUSIONS:

Mobility - Laboratory Volatility

1. The portion of this study investigating the volatilization of chlorpyrifos from corn is scientifically valid; however, the portion of this study investigating the volatilization of chlorpyrifos from soil cannot be validated because the soil was not sampled immediately after treatment to confirm the application rate and no data on the trapping efficiency of the polyurethane foam plugs were provided, thus, the concentration of residues volatilized could not be determined. ←
2. [¹⁴C]Chlorpyrifos residues volatilized with a half-life of <12 hours from the surface of corn leaves treated with formulated (4 lb/gal, EC) [¹⁴C]chlorpyrifos at 1.12 kg/ha. At 96 hours posttreatment, >80% of the applied radioactivity had been volatilized, and ~1 and 11% of the applied was detected on the leaf surfaces and in the leaf tissues, respectively.
3. This study does not fulfill EPA Data Requirements for Registering Pesticides because: Experiment 1 - volatility data were not expressed as $\mu\text{g}/\text{cm}^2/\text{hour}$, air concentrations were not expressed as $\mu\text{g}/\text{m}^3$ or mg/m^3 ,

the test soils were not completely characterized, and the relative humidity was not reported; Experiment 2 - volatility data were not expressed as $\mu\text{g}/\text{cm}^2/\text{hour}$, air concentrations were not expressed as $\mu\text{g}/\text{m}^3$ or mg/m^3 , and material balances were incomplete.

MATERIALS AND METHODS:

Experiment 1

Samples of moistened (100% of 1/3 bar) loam, sandy loam, and silty clay loam soils (Table 1) were placed in a volatility apparatus (Figures 1 and 2) and surface-treated with acetone solutions of 2,6-pyridine ring-labeled [^{14}C]chlorpyrifos (radiochemical purity 98.8%, specific activity 1.99 mCi/mmol, Dow Chemical Co.) at 6 ppm (1.12 kg/ha). The soil samples were maintained at 25°C, and water-saturated air was passed over the soil at an airflow rate of 1.0 L/minute (1.0 km/hour wind speed). Volatilized compounds were trapped with polyurethane foam plugs ($\sim 0.032 \text{ g}/\text{cm}^3$ density).

Polyurethane foam plugs were periodically sampled and extracted with acetone. Radioactivity in the extract was quantified using LSC.

Experiment 2

Jacques JX-21 field corn plants (24 plants, ~ 35 cm tall) were contained in an enclosed glass environmental chamber (Figure 3), and an aqueous solution of 2,6-pyridine ring-labeled [^{14}C]chlorpyrifos (radiochemical purity >99%, specific activity 14.2 mCi/mmol, Dow Chemical Co.) formulated as Lorsban (4 lb/gal EC) was applied at 1.12 kg/ha to one leaf on each plant. The chamber was maintained at 30°C, with a relative humidity of 45-65%, and a photoperiod of 15 hours on:9 hours off (1000 W G.E. Duro-glow lamp above the chamber). Air was passed through the chamber at a rate of 0.8 km/hour. Volatile compounds were trapped with polyurethane foam plugs. Foam plugs and treated leaves were sampled at 0, 3, 6, 9, 12, 24, 48, and 96 hours posttreatment.

Polyurethane foam plugs were extracted with acetone, and radioactivity in the extract was quantified using LSC. Leaf samples were washed with methanol, and [^{14}C]residues in the washes were quantified using LSC. [^{14}C]Residues remaining in the leaf tissue were quantified by LSC following combustion.

REPORTED RESULTS:

Experiment 1

Physical properties of chlorpyrifos are presented in Table 2. [^{14}C]-Chlorpyrifos residues volatilized with half-lives of >36, 29, and 32 hours from loam, sandy loam, and silty clay loam soils, respectively, treated with [^{14}C]chlorpyrifos at 6 ppm. At 36, 29, and 32 hours post-treatment, ~ 62 , 89, and 62% of the applied radioactivity remained on the loam, sandy loam, and silty clay loam soils, respectively (Table 3).

Experiment 2

[¹⁴C]Chlorpyrifos residues volatilized with a half-life of <12 hours from corn plants treated with formulated [¹⁴C]chlorpyrifos at 1.12 kg/ha. At 96 hours posttreatment, >80% of the applied radioactivity had been volatilized and ~1 and 11% of the applied was detected on the leaf surfaces and in the leaf tissues, respectively (Table 4).

DISCUSSION:

General

1. Volatility data were not expressed as $\mu\text{g}/\text{cm}^2/\text{hour}$.
2. Air concentrations were not expressed as $\mu\text{g}/\text{m}^3$ or mg/m^3 .

Experiment 1

1. The soil was not sampled immediately after treatment to confirm the stated chlorpyrifos application rate.
2. No data on the trapping efficiency of the polyurethane foam plugs were provided. The study authors did state that a preliminary experiment was conducted in which chlorpyrifos was applied directly to a foam plug and air was passed through the plug for 2 days, and the test substance was retained on the foam plug.
3. The CEC of the soils was not reported.
4. According to the USDA Soil Textural Classification System, the soil identified as a sandy clay loam is a silty clay loam. The correct classification is used in describing the soil throughout the study.
5. The relative humidity was not reported.

Experiment 2

Material balances were incomplete at the 3-, 6-, and 9-hour sampling intervals.

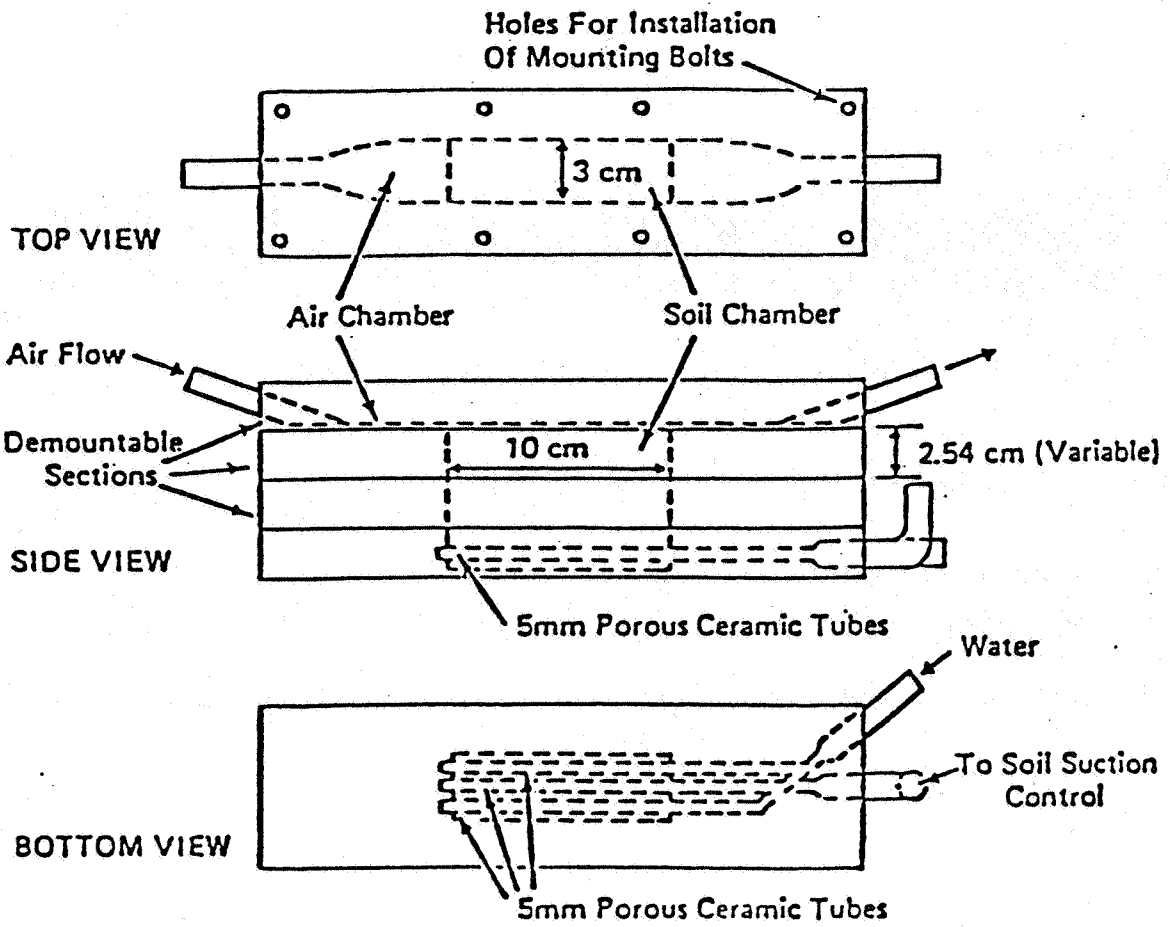


Figure 1. Diagram of soil volatility apparatus.

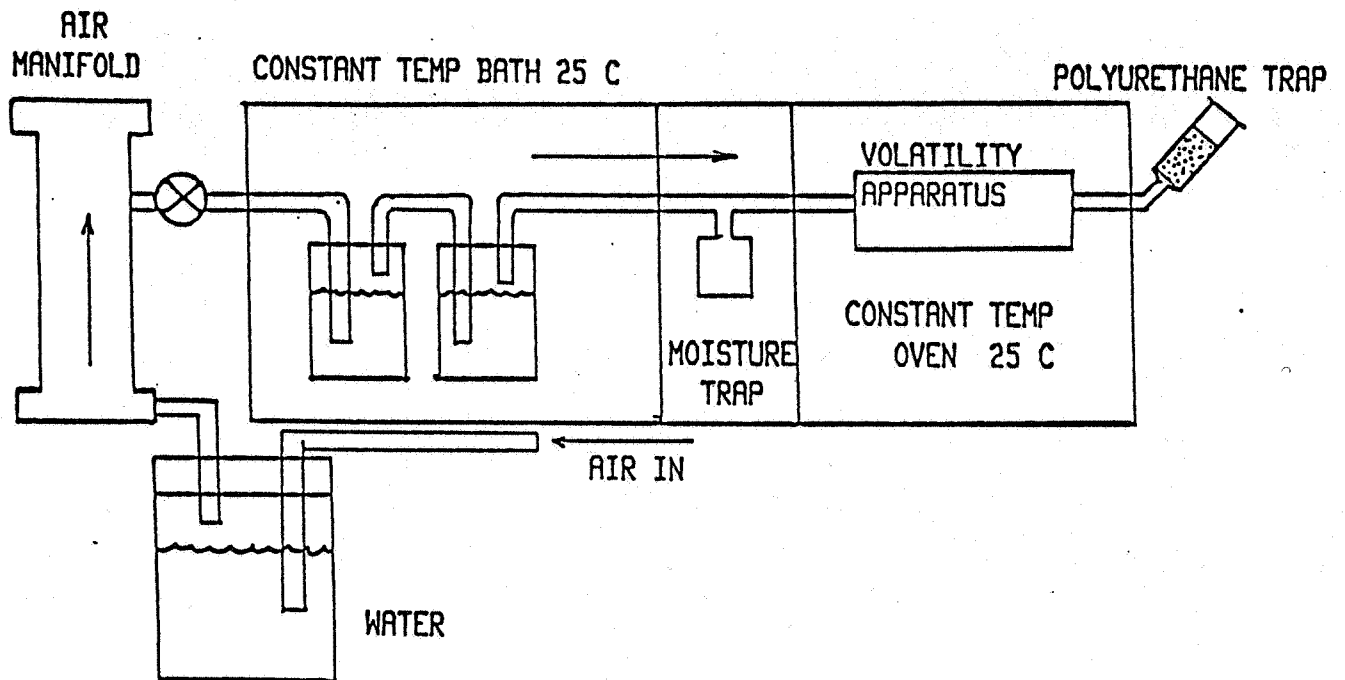


Figure 2. Diagram of soil volatility system.

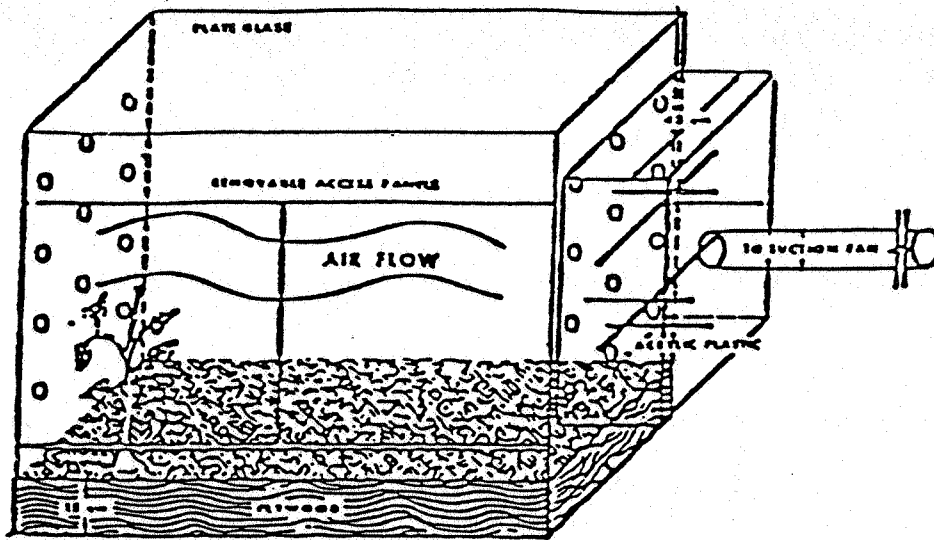


Figure 3. Diagram of plant volatility chamber.

Table 1. Soil characteristics.

Soil type	Location	Sand	Silt	Clay	Organic matter	pH
		%				
Commerce loam	Mississippi	38	48	14	0.68	6.7
2:2 ^a sandy loam	Germany	78	12	10	2.63	6.2
Kawkawlin silty clay loam ^b	Michigan	12	60	28	1.46	6.4

^a German standard soil.

^b Reported to be a sandy clay loam; however, according to the USDA Soil Textural Classification System, the soil was determined to be a silty clay loam.

Table 2. Physical properties of chlorpyrifos.

Molecular weight	350.6 g/mol
Water solubility	1.07 ppm ^a
Vapor pressure	1.9 x 10 ⁻⁵ torr at 25°C ^b
Soil sorption constant, K _{oc}	6000 - 10000 ^c

^a Swann, R.L., D.A. Laskowski, P.J. McCall, K. Vander Kay, and H.J. Dishburger. 1983. A rapid method for the estimation of the environmental parameters octanol/water partition coefficient, soil sorption constant, water to air ratio, and water solubility. Residue Rev. 85, 17-26.

^b Burst, H.F. 1966. A summary of chemical and physical properties of Dursban. Down to Earth, Winter, 21.

^c McCall, P.J., G.R. Oliver, and R.L. McKeller. 1984. Modeling the runoff potential of chlorpyrifos in a terrestrial - aquatic watershed. GH-C 1694. Unpublished report of the Dow Chemical Company.

Table 3. [¹⁴C]Chlorpyrifos residues (% remaining)^a on loam, sandy loam, and silty clay loam soils treated with ring-labeled [¹⁴C]chlorpyrifos at 6 ppm.

Sampling interval (hours)	Loam soil	Sampling interval (hours)	Sandy loam soil	Sampling interval (hours)	Silty clay loam soil ^b
0.0	100.0	0.0	100.0	0.0	100.0
2.5	98.2	3.0	99.0	2.0	98.2
7.0	93.5	6.0	97.5	4.0	95.2
10.5	88.6	8.0	96.6	8.5	88.8
24.0	71.4	23.0	90.5	24.0	70.1
36.0	62.2	29.0	88.7	32.0	62.0

a Calculated from the difference between the amount of radioactivity volatilized and that theoretically applied to the soil. The amount of radioactivity volatilized was determined by dividing the total radioactivity extracted from the polyurethane foam plugs by the amount of radioactivity theoretically applied to the soil.

b Classified by the study authors as a sandy clay loam.

Table 4. [¹⁴C]Chlorpyrifos residues (% of applied) in and on leaf tissue and in air after corn plants were treated with [¹⁴C]chlorpyrifos formulated as Lorsban (4 lb/gal, EC) at 1.12 kg/ha.

Sampling interval (hours)	Leaf tissue			Total [¹⁴ C]
	Surface extractable ^a	Unextractable	Volatiles	
0	100	---	---	100.0
3	44.7	15.3	22.5	82.5
6	20.9	21.1	36.7	78.7
9	16.0	24.1	48.7	88.8
12	6.6	28.7	56.8	92.1
24	5.8	21.5	72.0	99.3
48	1.8	17.0	79.3	98.1
96	1.1	10.6	84.2	95.9

^a Methanol wash.

EXECUTIVE SUMMARY

The data summarized here are scientifically valid data that have been reviewed in this report but do not fulfill data requirements unless noted in the Recommendations section of this report.

2,6-Pyridine ring-labeled [¹⁴C]chlorpyrifos (purity 97.9%), at ~0.6 ppm, degraded with calculated half-lives of 72.8 days at pH 5, 72.1 days at pH 7, and 15.8 days at pH 9 in sterile buffered solutions incubated in the dark at 25°C for 35 days (McCall, 1986; No MRID). Two degradates were formed and were identified as 3,5,6-trichloro-2-pyridinol and O-ethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate.

[¹⁴C]Chlorpyrifos (purity >98%) was slightly mobile to mobile in sandy loam, loam, and silt loam soils, based on batch equilibrium and column leaching studies (McCall, 1985b; No MRID). The adsorption and leaching of [¹⁴C]chlorpyrifos were positively affected by the organic carbon content of the soil. Adsorption coefficients (K_d) ranged from 49.9 in a loam soil (organic carbon content 0.68%) to 99.7 in a silt loam soil (organic carbon content 2.01%). In soil columns, ~5% of the applied chlorpyrifos leached below the upper 5 cm in the loam soil, while <1% of the applied chlorpyrifos leached below the upper 5 cm of the sandy loam and silt loam soils (the two soils highest in organic carbon).

2,6-Pyridine ring-labeled [¹⁴C]chlorpyrifos (purity 97.9%), at 1.2 ppm, in a sandy loam soil maintained under aerobic conditions at 25°C in the dark, degraded with a half-life of 7-10 days (McCall, 1985a; No MRID). One major degradate, identified as 3,5,6-trichloro-2-pyridinol, was formed (maximum 28.1% of the applied at 10 days posttreatment).

Aged (10 days) 2,6-pyridine ring-labeled [¹⁴C]chlorpyrifos (purity 97.9%) residues were moderately mobile in a sandy loam soil after leaching with 20 inches of water; 73% of the applied residues remained in the upper 5 cm of the column (McCall, 1985a). The remaining [¹⁴C]residues were distributed evenly throughout the column and in the column leachate. Chlorpyrifos and 3,5,6-trichloro-2-pyridinol were the major components of the residues. 3,5,6-Trichloro-2-pyridinol (purity 99%) had adsorption coefficients (K_d) of 0.37 and 0.33 in two different samples of the sandy loam soil.

[¹⁴C]Chlorpyrifos residues volatilized with a half-life of <12 hours from the surface of corn leaves treated with formulated (4 lb/gal EC) [¹⁴C]chlorpyrifos at 1.12 kg/ha (McCall et al., 1985). At 96 hours posttreatment, >80% of the applied radioactivity had been volatilized, and ~1 and 11% of the applied was detected on the leaf surfaces and in the leaf tissues, respectively.

RECOMMENDATIONS

Available data are insufficient to fully assess the environmental fate and transport of, and the potential exposure of humans and nontarget organisms to chlorpyrifos. The submission of data relevant to registration requirements (Subdivision N) for terrestrial food crop, terrestrial nonfood, aquatic nonfood crop, domestic outdoor, and indoor use sites is summarized below:

Hydrolysis studies: One study (McCall, 1986; No MRID) was reviewed and is scientifically valid. This study fulfills data requirements by providing information on the hydrolysis of chlorpyrifos at pH 5, 7, and 9.

Photodegradation studies in water: No data were reviewed for this addendum, but all data are required.

Photodegradation studies on soil: Based on data submitted for the Chlorpyrifos Addendum dated April 24, 1985, all data requirements have been met.

Photodegradation studies in air: No data were submitted for this addendum, but all data are required. Reference is made to conclusions reached following earlier reviews of similar studies.

Aerobic soil metabolism studies: Based on data submitted for the Chlorpyrifos Registration Standard dated September 28, 1984, all data requirements have been met.

Anaerobic soil metabolism studies: Based on data submitted for the Chlorpyrifos Registration Standard dated September 28, 1984, all data requirements have been met.

Anaerobic aquatic metabolism studies: Based on data submitted for the Chlorpyrifos Addendum dated April 24, 1985, all data requirements have been met.

Aerobic aquatic metabolism studies: No data were reviewed for this addendum, but all data are required.

Leaching and adsorption/desorption studies: Two studies were reviewed; both were considered scientifically valid. One study (McCall, 1985b; No MRID) partially fulfills data requirements by providing information on the leaching of unaged chlorpyrifos through columns of three soils and on the adsorption of chlorpyrifos to three soils. The second study (McCall, 1985a; No MRID) partially fulfills data requirements by providing information on the leaching of aged chlorpyrifos residues through one soil. Based on the Chlorpyrifos Registration Standard and Addenda, data have been reviewed which provide information on the adsorption of chlorpyrifos (unaged) to a variety of soils and an aquatic sediment, and on the leaching of unaged chlorpyrifos through three soils and aged chlorpyrifos through one soil. A study is needed providing either information on the desorption of chlorpyrifos from four soils and one sediment, or on the leaching of unaged chlorpyrifos through one additional soil and one sediment. Reference is made to conclusions/recommendations reached following earlier reviews of similar studies.

Laboratory volatility studies: One study (Swann et al., 1985; No MRID) was reviewed and is scientifically valid. This study does not fulfill data requirements because: Experiment 1 - volatility data were not expressed as $\mu\text{g}/\text{cm}^2/\text{hour}$, air concentrations were not expressed as $\mu\text{g}/\text{m}^3$ or mg/m^3 , the test soils were not completely characterized, and the relative humidity was not reported; Experiment 2 - volatility data were not expressed as $\mu\text{g}/\text{cm}^2/\text{hour}$, air concentrations were not expressed as $\mu\text{g}/\text{m}^3$ or mg/m^3 , and material balances were incomplete. All data are required.

Field volatility studies: No data were reviewed for this addendum; however, all data may be required depending upon the results of the laboratory volatility studies.

Terrestrial field dissipation studies: No data were reviewed for this addendum, but all data are required.

Aquatic field dissipation studies: No data were reviewed for this addendum, but all data are required.

Forestry dissipation studies: No data were reviewed for this addendum; however, no data are required because chlorpyrifos has no forestry uses.

Dissipation studies for combination products and tank mix uses: No data were reviewed for this addendum; however, no data are required because data requirements for combination products and tank mix uses are currently not being imposed.

Long-term field dissipation studies: No data were reviewed for this addendum; however, based on data submitted for the Chlorpyrifos Registration Standard dated September 28, 1984, the data which were submitted for aerobic soil metabolism meet this requirement.

Confined accumulation studies on rotational crops: No data were reviewed for this addendum, but all data are required.

Field accumulation studies on rotational crops: No data were reviewed for this addendum, but all data are required.

Accumulation studies on irrigated crops: No data were reviewed for this addendum, but all data are required.

Laboratory studies on pesticide accumulation in fish: No data were reviewed for this addendum, but all data are required.

Field accumulation studies of aquatic nontarget organisms: No data were reviewed for this addendum, but all data may be required depending upon results of fish accumulation studies

Reentry: No data were reviewed for this addendum, but all data may be required. California has imposed a reentry interval of 2 days for crops; a Federal reentry interval of 1 day for crops has been established. For each representative crop/site the registrant is required to propose an acceptable interval based on either: a) data on dissipation of foliar and/or soil residues of chlorpyrifos (decline curve), on human exposure to those residues, and on toxicity of chlorpyrifos; or b) determination of that time beyond which there are no detectable, dislodgeable residues remaining in the worker environment.

REFERENCES

McCall, P.J. 1985a. Chlorpyrifos aged column leaching study. Report GH-C 1778. Submitted by Dow Chemical U.S.A, Agricultural Products Department, Midland, MI. Acc. No. 260794. Reference 3.

McCall, P.J. 1985b. Column leaching and sorption studies with chlorpyrifos. Report GH-C 1777. Submitted by Dow Chemical U.S.A., Agricultural Products Department, Midland, MI. Acc. No. 260794. Reference 2.

McCall, P.J. 1986. Hydrolysis of chlorpyrifos in dilute aqueous solution. Report GH-C 1791. Submitted by Dow Chemical U.S.A., Agricultural Products Department, Midland, MI. Acc. No. 260794. Reference 1.

McCall, P.J., R.L. Swann, and W.R. Bauriedel. 1985. Volatility characteristics of chlorpyrifos from soil and corn. Submitted by Dow Chemical Co., Midland, MI. Acc. No. 260794. Reference 4.

APPENDIX