

Shaughnessy No.: 059101

Date Out of EFGWB: 7/10/91

TO: J. Edwards
Product Manager # 74
Registration Division (H7505C)

FROM: Michael R. Barrett, Acting Head
Ground-Water Technology Section
Environmental Fate & Ground-Water Branch/EFED (H7505C)

THRU: Henry Jacoby, Chief
Environmental Fate & Ground-Water Branch/EFED (H7507C)

Attached, please find the EFGWB review of:

Reg./File #: ID = 464-404

Chemical Name: Chlorpyrifos

Type Product: insecticide

Product Name: Dursban®, Lorsban®

Company Name: DOW Chemical Corporation

Purpose: Comment on the detection limit and analytical method used
for chlorpyrifos and 3,5,6-trichloro-2-pyridinol degradate

Date Received : 10/31/89

Action Code: 660

Date Completed: 5/20/91

EFGWB # (s): 90-0048

Monitoring study requested: _____

Total Review Time: 2-days

Monitoring study voluntarily: _____

Deferrals To: ☒ Ecological Effects Branch

☐ Science Integration and Policy Staff, EFED

☐ Non-Dietary Exposure Branch, HED

☐ Dietary Exposure Branch, HED

☐ Toxicology Branch I, HED

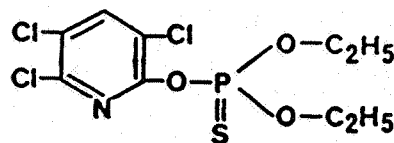
☐ Toxicology Branch II, HED

1. CHEMICAL: Common name: chlorpyrifos

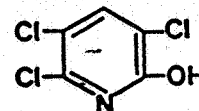
Chemical name: O,O-Diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate

Trade name: Dursban®, Lorsban®

Structure:



major degradate

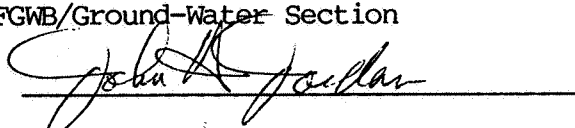


2. TEST MATERIAL: N/A

3. STUDY/ACTION TYPE: Comment on the registrant's detection limit and analytical method used to detect chlorpyrifos and the major degradate

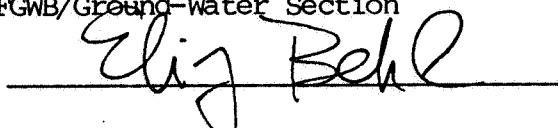
4. STUDY IDENTIFICATION: The attached October 9, 1989 memorandum, item V., outlines the registrant's objections to comments by Agency reviewers concerning their high detection limits.

5. REVIEWED BY:

John H. Jordan, Ph.D.
Microbiologist
OPP/EFED/EFGB/Ground-Water Section
Signature: 

Date: 5/21/91

6. APPROVED BY:

Elizabeth Behl, Acting Head
OPP/EFED/EFGB/Ground-Water Section
Signature: 

Date: 7/10/91

7. CONCLUSIONS:

Monitoring data indicate that chlorpyrifos residues exist in ground water below 50 ppb. Although the registrant, and others, have been using a classical analytical method with a minimum detection limit (MDL) of 50 ppb, there are now EPA approved analytical methods with MDLs at the 1 ppb or sub-ppb level for chlorpyrifos parent and the major degradate TCP in water and soil. The methods are referenced in the Recommendations Section.

Although deficiencies exist in the data base, there is sufficient information to indicate that chlorpyrifos is not likely to leach to ground water. The parent material is moderately persistent but relatively immobile. Chlorpyrifos has been monitored in several states, e.g., California and Florida but no validated detections have been reported. The major degradate, TCP, however, is mobile and moderately persistent in soil; consequently, TCP has a potential to reach ground water. TCP (3,5,6-trichloro-2-pyridinol) has not been monitored and consequently there is no data base.

2

The Ecological Effects Branch (EEB) indicated that chlorpyrifos is extremely toxic to aquatic organisms, e.g., the LC₅₀ for the marine invertebrate mysid shrimp is 0.035 ppb. Therefore, it will be necessary to lower the minimum detection limit (MDL) in order to monitor for the low residue levels that affect some aquatic organisms. We defer to EEB to specify limits of detection required to monitor for residues in specific aquatic organisms.

On March 18, 1991 we were informed by Elizabeth Doyle, Section Chief, Toxicology Branch II, that the TCP degradate is of no toxicological concern (to humans) and will not be included in the food tolerance.

8. RECOMMENDATIONS:

There are three EPA approved methods of analysis:

- (a) for Chlorpyrifos - Method No. 507 or 508. (NPS methods # 1 and 2)
- (b) for TCP (the major degradate) method No. 515.1 (NPS method # 3)
(exclude the hydrolysis step)

The above methods were used by EPA in the National Pesticide Survey (NPS) and are available for use by the registrant. For water analysis, using the EPA validated methods, MDLs and limits of quantitation should be much less than 20 ppb for chlorpyrifos and 50 ppb for TCP reported by the registrant. For ground-water pesticide residues the Ground-Water Section prefers that MDLs for soil be down to at least 5 ppb, or lower if possible; for residues in water 0.1 - 0.2 ppb, or lower is preferred. Monitoring aquatic organisms will require lowering the MDLs from 50 ppb to below one ppb; EEB will give the registrant appropriate guidelines for monitoring aquatic sites. The EPA Bay ST. Louis (Mississippi) laboratory can verify (validate) the registrant's new methods for chlorpyrifos and TCA.

Analytical Methods References

NPS # 1 (Method No. 507)

Determination of N and P Containing Pesticides in Water by GC with N/P detection. Revision 2.0, EPA, EMSL R&D, Cincinnati, Ohio.

NPS # 2 (Method 508)

Determination of Chlorinated Pesticides in Water by GC with Electron Capture detection. Revision 3.0, EPA, EMSL R&D, Cincinnati, Ohio.

NPS #3 (Method No. 515.1)

Determination of Chlorinated Acids in Water by GC with Electron Capture Detection. EPA, EMSL R&D, Cincinnati, Ohio.

9. BACKGROUND:

A. Introduction

The K_ds in three soils ranged from 50 to 100 for chlorpyrifos and K_{oc}s averaged 6000. Only 0.3 to 1.3 % of the radioactivity appeared in the eluate from three soils. The half-life of the parent ranged from 33 to 56 days for 3 soils. In contrast, a K_d for the TCP degradate was 0.35; the half-life was similar to the parent. The anaerobic half-life was approximately one year.

The registrant contends that since the parent does not have a potential to leach into ground water and the TCP degradate is of no toxicological concern, there is no need to lower the detection and quantitation limits to monitor residues in soil and water. However, EFGW Branch is charged with monitoring for residues even though there is little or no toxicological concern, at present. Interactions of ground-water residues could change some innocuous chemical residue moieties into hazardous compounds even though some interactants (residues) may have been of little or no toxicological concern. Also, present biological methods of testing for toxicological effects are not always effective indicators for all chemicals. It is much safer and more cost effective to keep residues out of ground water than to remove them.

B. Directions For 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 greenhouse), lawns and ornamental turf, domestic outdoor and indoor sites, commercial establishments, (edible and nonedible product areas), aquatic non-crop sites, terrestrial non-crop sites, and poultry, pet, and animal housing, and on beef cattle and dogs. Chlorpyrifos is also used as a seed treatment.

Of the total domestic chlorpyrifos usage, 57% is applied to corn and 5-6% to cotton. Commercial pest control and lawn and garden services comprise 20-22% of annual chlorpyrifos consumption followed by domestic household and lawn and garden use (9-13%). Application rates range from 0.1 oz ai/A for some seed treatments to 50 lbs ai/A for certain tree fruit applications.

10. DISCUSSION:

Regardless of the toxicology profile, the Environmental Fate and Ground-Water Branch is charged with determining the potential of registered pesticides and their degradate residues to reach ground water.

Current methods of analysis for numerous pesticide residues in water can accurately quantitate residues below 0.1 ppb. A similar detection/quantitation limit for TCP and parent in the ground-water matrix can also be developed by modifying the EPA methods referenced in the Recommendations Section. Mr. Bob Maxey, The EPA Bay St. Louis Laboratory, indicated they are confident that a method for detecting sub-ppm levels can be developed. The methods used or developed by the registrant to detect and quantify parent and TCP, at or below the claimed levels, must be validated by an Agency lab.

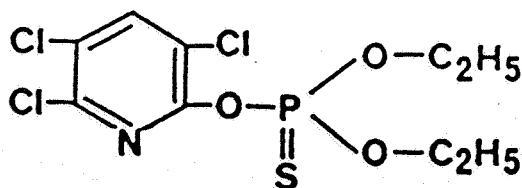
In the attached letter the registrant stated that 50 ppb is the accepted MDL for determining TCP in water. However, analytical methods for TCP and chlorpyrifos referenced in the Recommendations Section detect and quantitate parent and TCP at the ppb or sub-ppb level.

According to a facsimile (FAX) received from Ms. Pat Nugent of Dow Elanco on 1/24/91, Dow uses a 1984 method for TCP titled: McKellar, R.L. and W.C. Brown. Determination of Triclopyr and 3,5,6-trichloro-2-pyridinol in Water by Gas Chromatography. A gas chromatographic method must be confirmed by mass spectrometry but the method we received from Dow did not indicate that a mass spectrometer was used. As the registrant indicated, background must be subtracted when using prepared standards and GC.

4

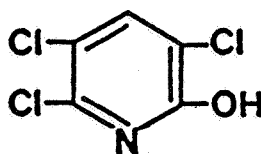
4.

If the registrant will use the methods specified in this action, the Agency believes that Dow Elanco will be able to detect and quantify parent chlorpyrifos and the major degradate TCP at the ppb or sub-ppb level.

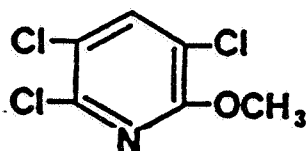


chlorpyrifos

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



3,5,6-Trichloro-2-pyridinol



3,5,6-Trichloro-2-methoxypyridine

Chlorpyrifos and its metabolites.

Code	Structure	Chemical Name
I		0,0-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate (chlorpyrifos)
II		0,0-diethyl O-(3,6-dichloro-2-pyridyl)phosphorothioate
III		0,0-diethyl O-(dichloro, methylthio, 2-pyridyl)phosphorothioate
IV		O-ethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate
V		O-ethyl O-(3,5,6-trichloro-2-pyridyl)phosphate
VI		S-ethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate
VII		3,5,6-Trichloro-2-pyridyl phosphate
VIII		3,5,6-Trichloro-2-pyridinol
IX		Diethyl thionophosphate
X		Diethyl phosphate

^aThe exact position of the thiomethyl group was not determined; however, it was determined that the group is located at either position 2 or 5 on the ring.

Use this form for individual studies & to submit pesticide applications.



United States Environmental Protection Agency
Office of Pesticide Programs
Washington, DC 20460

Data Review Record

Confidential Business Information - Does not contain
National Security Information (E.O. 12065)

Pack Number

Date Received

49795

EFED

10-31-89

1. Product Name

chl. py. 16

Chemical Name

chl. py. 16 059101-6

2. Identifying Number	3. Record Number	4. Action Code	5. MRID/ Accession Number	6. Study Guideline or Narrative
414-404	254308	660		

7. Reference No.	8. Date Rec'd (EPA)	9. Prod/Review Mgr/DCI	10. PM/RM Team No.	11. Date to HED/ EFED/RD/BEAD	12. Proj Return Date	13. Date Returned to RD/SRRD
1	10-17-89	J. EDWARDS	74		11-30-89	30-2-85

Instructions

DATA (chl. py. 16) Standard
form for review V
to HED.
Attn: P. Hutton / M. E. Smith

This Section Applies to Review of Studies Only

14. Check Applicable Box ☐ Adverse 6(a)(2) Data (405) ☐ Special Review Data (670) ☐ Generic Data (Reregistration) (660) ☐ Product Specific Data (Reregistration) (655)				15. No. of Individual Studies Submitted		
16. Have any of the above studies (in whole or in part) been previously submitted for review? ☐ Yes (Please identify the study(ies)) ☐ No				17. Related Actions		
18.	To	Type of Review	19. Reviews Also Sent to		20. Data Review Criteria	
HED		Science Analysis & Coordination	☐ SAC	☐ PC	A. Policy Note No. 31 ☐ 1 = data which meet 6(a)(2) or meet 3(c)(2)(B) flagging criteria ☐ 2 = data of particular concern from registration standard ☐ 3 = data necessary to determine tiered testing requirements	
		Toxicology/HFA	☐ TOX/HFA	☐ PL		
		Toxicology/IR	☐ TOX/IR	☐ EA		
		Dietary Exposure	☐ DEB	☐ AC		
EFED		Nondietary Exposure	☐ NDE	☐ BA	B. Section 18 ☐ 1 = data in support of section 3 in lieu of section 18	
		Ecological Effects	☐ EEB			
SRRD		Environmental Fate & Groundwater	☐ EFGWB			C. Inert Ingredients ☐ 1 = data in support of continued use of List 1 inert
		Special Review				
		Reregistration	☐ SR			
RD		Generic Chemical Support	☐ RER			
		Insecticide-Rodenticide	☐ GSC			
		Fungicide-Herbicide				
		Antimicrobial	☐ IR			
BEAD		Product Chemistry	☐ FH			
		Precautionary Labeling	☐ AM			
		Economic Analysis				
		Analytical Chemistry				
		Biological Analysis				

☐ Confidential Statement of Formula (EPA Form 8570-4) Attached (Trade Secrets)

☐ Label Attached

8