

US EPA ARCHIVE DOCUMENT

1. CHEMICAL:

Common Name: Chlorethoxyfos

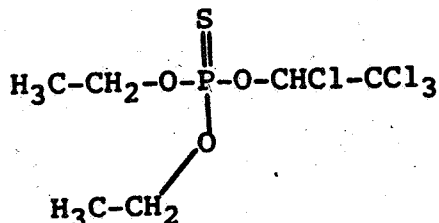
Trade Name: Fortress

(Labeled for T band and in-furrow application only)

Chemical Name: phosphorothioic acid, O,O-diethyl O-(1,2,2,2-tetrachloroethyl) ester]

Type of product: Soil Insecticide

Chemical Structure:



Physical/Chemical Properties

molecular weight: 336

CAS registry No: 54593-83-8

Boiling point: 105 to 115 C at 0.8 mmHg.

aqueous solubility: at 25 C was reported to be 2.1 ppm.

vapor pressure: 1.7×10^{-3} mm Hg at 25 C.

Henry's law constant: 1.5×10^{-2} , 3.5×10^{-4} atm m³ mole⁻¹

Kow = 39,000

Koc = 6100 (average on four soils)

pH = 3.52

U.V. max. = <290 nm

2. TEST MATERIAL:

See attached DERS.

3. STUDY/ACTION TYPE:

To review data to support the registration of the 2.5 and 5G granular on Field, Sweet and Pop corn as well as supplemental data to an anaerobic aquatic metabolism (162-3) study, and a field volatility (163-3) study.

4. STUDY IDENTIFICATION:

(1) MRID No:43607301

L. Somasundaram. (SUPPLEMENTAL INFORMATION) Anaerobic Metabolism of ¹⁴C-DPX-43898 in Soil. January 18, 1995. Performed by E.I. du Pont de Nemours and Company, Dupont Agricultural Products, Global Technology Division, Experimental Station, Wilmington, Delaware 19880-0402. ID AMR 1456-89

(2) Application for Registration of the Dupont Fortress 2.5G and 5G granular insecticide including proposed label.

(3) MRID No: 43550307

D. Larry Merricks, Michael P. Jensen. December 14, 1994. Chlorethoxyfos Field Volatility Study. Performed by Agrisearch Incorporated 5734 Industry Lane Fredrick MD 21701. Sponsored by

E.I. du Pont de Nemours and Company Dupont Agricultural Products
Dupont Experimental Station Wilmington DE 19880-0402. Laboratory
ID Agrisearch Project No. 1719, Dupont Protocol No. AMR 2315-92.

5. REVIEWED BY:

Kevin L. Poff, Chemist
Environmental Chemistry Review Section #3
Environmental Fate and Groundwater Branch/EFED

Kevin Poff
Date: JUL 12 1995

6. APPROVED BY:

Akiva Abramovitch, Ph.D., Chemist
Environmental Chemistry Review Section #3
Environmental Fate and Groundwater Branch/EFED

Akiva Abramovitch
Date: JUL 12 1995

7. CONCLUSIONS:

a) All data requirements for the registration of Dupont's Fortress 2.5 and 5% granular insecticide have been satisfied with the exception of the Field Volatility (163-3) study (MRID #43550307) which may be upgraded to an acceptable level with the submission of additional data (see discussion section and DER).

b) Laboratory and field data indicate that the potential of chlorethoxyfos to contaminate ground water is low, due mainly to the compounds high adsorptivity to soil, its low water solubility and short field dissipation half-lives.

c) The supplemental information (MRID #43607301) submitted to address questions raised in a previously reviewed Anaerobic Metabolism of ¹⁴C-DPX-43898 in Soil is adequate to upgrade the previously reviewed study MRID #41736825 from ancillary to acceptable.

EXECUTIVE SUMMARY: ENVIRONMENTAL FATE, GROUND AND SURFACE WATER ASSESSMENT

Chlorethoxyfos has a very low potential to contaminate ground water due to its high adsorptivity to soils, its low water solubility and rapid field dissipation half-lives.

Adsorption/Desorption (163-1), terrestrial field (164-1) and field volatility (163-3) studies indicate rapid dissipation half-lives with low mobility in soil. Dissipation in soil is through microbial processes yielding trichloroacetaldehyde then CO₂. Field volatility studies have shown that volatilization is also a dissipation mechanism as field half-lives are substantially less than those obtained in laboratory studies minimizing volatilization. Soil conditions seem to strongly affect the volatilization of the compound, i.e., higher soil moisture the higher the rate, higher soil organic matter lowers the rate of volatilization. Highest air concentrations for chlorethoxyfos are measured 48 hours after application.

Terrestrial field studies conducted with the preemergence soil-incorporated band over-row application of 10G formulated product at exaggerated use rates (3X; 0.5 lb ai/A) showed rapid dissipation times: the dissipation half-life of chlorethoxyfos in the top 3 inches of an Iowa loam soil was 2.0 days; for chlorethoxyfos in the top 3 inches of an Illinois clay loam soil, the study authors calculated an initial dissipation half-life of 2.6 days; in California the half-life was 7-14 days in a sandy loam soil and 14-35 days in a clay loam soil in Iowa. Another sandy loam in North Carolina gave a half-life range of 14-48 days from the upper 3 inches. In addition, field half-lives from measured concentrations of chlorethoxyfos in soil from field volatility studies have compared well to the terrestrial studies with calculated half-lives of 29 and 8 days at two separate sites.

Chlorethoxyfos does have the potential to runoff to surface water through erosion of soil particles to which the compound is adsorbed, but rapid dissipation of the compound in soil and soil incorporation will decrease availability of chlorethoxyfos for runoff. If the compound were to reach surface water it may persist for some time due to the relatively long abiotic hydrolysis half-lives (pH 5 and 7, 72 and 59 days respectively) as well as the low inclination to photodegrade. If the compound were to reach surface water it would also have a very high potential to bioaccumulate (maximum BCF's of 1000-4000), however the chemical would dissipate rapidly from the exposed tissues due to rapid depuration. In addition, if the compound were to reach surface waters volatilization would greatly decrease the persistence (Henry's law constant: two reported values, 1.5×10^{-2} , 3.5×10^{-4} atm m³ mole⁻¹).

8. RECOMMENDATIONS:

Inform the registrant that the EFGWB has sufficient data to assess the environmental fate of chlorethoxyfos with reference to the registration of Dupont's Fortress 2.5 and 5% granular insecticide. Additional data is required to supplement the reviewed Field Volatility (163-3) study as volatilization is an important mechanism in the dissipation of chlorethoxyfos in the environment.

9. DISCUSSION:

9.1 Anaerobic Aquatic Metabolism

Supplemental information has been submitted to address questions raised in a previously reviewed study (2/94; MRID #41736825, Anaerobic Metabolism of ¹⁴C-DPX-43898 in Soil. Woodward, M.D. and C.M. Pukalski) which was determined to be unacceptable due to the lack of the identification of volatiles present at 58.3% on Day 81.

Extraction procedures of the test samples were included (see attached) as well as a representative chromatogram. The extraction procedure resulted in a hexane/water partition where two samples were taken for quantitation of radioactivity by LSC. It was

determined that nearly 90% of the total radioactivity was present in the hexane fraction, so the water layer containing less than 7% of the applied radioactivity was not further analyzed by HPLC. Chlorethoxyfos was the only material detected in the hexane extract by HPLC.

9.2 Registration of the 2.5G and 5G Fortress

Dupont has requested registration of the new active ingredient Fortress in a 2.5% and 5% granular formulation. Dupont intends to sell the 2.5% granular in a bag for use by growers with conventional planters and Fortress 5% granular will be sold only in the enclosed tamper-proof Smartbox to mitigate worker exposure.

The 2.5% granular formulation as opposed to the 5% granular formulation reduces the label signal word from "Danger" to "Warning" because of the reduction of active and therefore in toxicity category from I to II. The proposed use rate for the 2.5G is 6 oz./1000 row feet and the use rate for the 5G will be 3 oz./1000 row feet equating to approximately 5.0 to 6.5 lb formulated product per acre or 0.125 to 0.163 lb. ai/A.

Previously reviewed terrestrial field dissipation studies have indicated chlorethoxyfos applied at an exaggerated rate (3X, 0.5 lb ai/A) dissipated fairly rapidly with low to moderate mobility. Chlorethoxyfos was applied as a preemergence soil-incorporated band over-row application of Fortress 10G in those EFGWB reviewed studies.

9.3 Field Volatility (163-3) DER 1

1. Study MRID #43550307 is unacceptable and does not currently satisfy the field volatility (163-3) data requirement for chlorethoxyfos for the following reason:

a) The registrant is required to calculate the evaporate flux which would give a more practical rate of volatilization with respect to time as opposed to instantaneous measurements.

2. Study MRID #43550307 may be considered supplemental until the registrant submits the required calculations.

3. Following the application at two separate sites of Fortress 5G (chlorethoxyfos; [phosphorothioic acid, O,O-diethyl O-(1,2,2,2-tetra chloroethyl) ester] at the maximum use rate of 6 oz. formulation per 1000 ft. (6.7 lb formulated product/acre; 0.168 lb ai/Acre) row to a bareground plot by T-banding to a depth of approximately 1.5-2 inches using a 4 row corn planter the volatilization of chlorethoxyfos in Oregon, MO was at a maximum (Table XII; Low volume filters) of 1692.42 pg/liter (7:15 pm) on day 0 at the 15 cm sampling height, then decreased significantly through day 11 where a maximum of 70.82 pg/liter (1:10 pm) was measured at the 15 cm air sampler. On day 12 and 13 the measured air concentrations of chlorethoxyfos at 15 cm increased again to

153.61 pg/liter and 146.25 pg/liter. The amount of chlorethoxyfos found in soil core samples was at a maximum of 2.18 ppm on day 0 then decreased to 1.62 ppm by day 13; the calculated soil half-life of chlorethoxyfos was 29 days.

In Bolckow, MO, with an identical application as above, in May of 1992, the volatilization of chlorethoxyfos was at a maximum (Table XII; Low volume filters, 15cm) of 68.71 pg/liter on day 0 then decreased slowly to 6.44 pg/liter by day 10. Air concentrations then increased to 122.33 pg/liter on day 12, then decreased to 62.55 pg/liter on day 13. The amount of chlorethoxyfos found in the soil slab samples was at a maximum of 0.89 ppm on day 0 then decreased slowly to 0.29 ppm by day 13; the calculated soil half-life of chlorethoxyfos was 8 days.

10. BACKGROUND :

Chlorethoxyfos (DPX-43898) is an organophosphorus insecticide currently being developed by du Pont for use in the control of corn root worms and other soil insects on corn. The proposed use rate is 0.3 oz ai/1000 feet of row (0.25 lb ai/A assuming 40-inch row spacing). Single active ingredient formulations include granular. Chlorethoxyfos is highly toxic to birds and fish. Chlorethoxyfos causes depression of cholinesterase.

This review addresses the new use application of the 2.5 and 5G granular on Field, Sweet, and Pop corn. The application rates are 6 oz. Fortress 2.5G/1000 row feet equivalent to 0.15 oz. ai/1000 ft. equivalent to 5 to 6.5 lb. Fortress 2.5G/A equivalent to 0.125 to 0.163 lb ai/A. Application will be at planting in furrow or T-band to control corn rootworm (Western, Northern, and Southern) cutworm, wireworm, seedcorn maggot, white grub, and symphylans. Fortress 5% granular will be sold only in the enclosed tamper-proof Smartbox to mitigate worker exposure and will be applied at 3 oz./1000 row feet equivalent to 0.125 to 0.163 lb ai/A.

The submission of data required for full registration of chlorethoxyfos on terrestrial food use sites is summarized below:

Satisfied:

-Hydrolysis (161-1); MRID #40883705, EFGWB #90-186, 1/31/89, EFGWB #90-0067, 2/21/90. Half-life of 72, 59 and 4.3 days at pH 5, 7, and 9 respectively at 25C. At pH 5 and 7 chloral hydrate was the major degradate, at pH 9 dichloroacetic acid.

-Photodegradation in Water (161-2); MRID #41736821, EFGWB #93-0258,-0259. Photodegraded with a half-life of 27 days (uncorrected for lamp intensity or continuous radiation) in sterile aqueous buffered solutions (pH 5) irradiated with a UV-filtered xenon light source at approximately 25 C. The dark control showed a half-life of 89 days when incubated in darkness under similar conditions. Degradates identified in the irradiated and dark control solutions were trichloroacetaldehyde (major degradate) and dichloroacetic

acid.

-*Photodegradation on Soil* (161-3); MRID #41736822, EFGWB #93-0258, -0259. The calculated half-life was 21 days for the irradiated (natural sunlight) and 26 days for the dark control. Non-irradiated samples produced chloral hydrate (43%), polar compounds (11%) and volatiles. The exposed samples produced chloral hydrate (17%), polar compounds (7%) and carbon dioxide (27%) and volatiles (1%).

-*Aerobic Soil Metabolism* (162-1); MRID #40883706, #41290617, EFGWB #90-186, 1/31/89, EFGWB #90-0067, 2/21/90. Based upon data from a static system the half-life of the parent was 20 days. Major degradates were chloral hydrate at a maximum of 21.9% of applied at day 5 then decreased to less than 5.1% at day 7. CO₂ increased throughout incubation time to greater than 47% of applied. Based upon data from a flow through system the half-life of the parent was 7 days. Although degradation to chloral hydrate and CO₂ contributed to the dissipation the volatilization of the parent contributed much more than the dissipation.

Ancillary data reviewed above: MRID #41736824, EFGWB #93-0258, -0259. The parent degraded with a half-life of approximately 23 days. Only chlorethoxyfos was identified in the soil; carbon dioxide was the major degradate and totaled 63.0% of the applied at 120 days posttreatment.

-*Anaerobic Soil Metabolism* (162-2); MRID #41736825, EFGWB #93-0258, -0259. Parent degraded with half-lives of 41-47 days in clay soil that was incubated anaerobically (flooding plus nitrogen atmosphere) in the dark at 25 °C for 62 days following 19 days of aerobic incubation. Only chlorethoxyfos was identified in the soil and floodwater; carbon dioxide was the major degradate and totaled 36.5% of the applied at the termination of the experiment. [¹⁴C]organic volatiles that comprised up to 58.3% of the applied (0.29 ppm) radioactivity were identified to be chlorethoxyfos. Study MRID #43607301. Volatiles present at 58.3% on Day 81 were identified to be mostly parent chlorethoxyfos where the hexane/water extract (hexane only as the water contributed only 7% of applied) was analyzed by HPLC.

- *Leaching/Adsorption/Desorption* (163-1); MRID #40883709, #41290618, EFGWB #90-186, 1/31/89, EFGWB #90-0067, 2/21/90. The Freundlich binding coefficients and the exponential constants for the adsorption of parent on a Hanford sandy loam (pH= 6.4, OM= 1.0%), North Carolina loamy sand (pH= 5.4, OM= 2.0%), Fargo silt loam (pH= 7.2, OM= 4.3%) and La Hogue (incorrectly identified as Flanagan) loam (pH= 7.4, OM= 5.0%) were K= 40, 1/n=1.1; K= 53, 1/n=1.1; K= 150, 1/n= 1.1; and K= 200, 1/n= 1.1. These results indicate that parent chlorethoxyfos is strongly bound to even low organic matter soils. The Freundlich binding coefficients and exponential constants for desorption of parent in the above soils are; K= 7.5, 1/n= 0.38; K= 8.2, 1/n= 0.39; K= 5.3, 1/n= 0.14; and K=5.2, 1/n= 0.12. These results indicate that parent chlorethoxyfos will not be easily desorbed after adsorption takes

place. Degradation was observed during the adsorption phase of the experiment with TCA being observed.

-Adsorption/Desorption (Batch Equilibrium on degradates); The Freundlich constants for the chloral hydrate and trichloroacetic acid were obtained from the literature and are less than 1 indicating that both have a high mobility potential.

-Leaching (soil column on chloral hydrate) A soil column leaching study from the literature also indicate that chloral hydrate is easily leached from the four test soils used indicating the high mobility of the compound.

-Laboratory Volatility (163-2); MRID #41736827, EFGWB #93-0258,-0259. The mass flux of chlorethoxyfos was measured at 45.6 cm².

-Terrestrial Field Dissipation (164-1); MRID # 41736828, MRID #41290619 (EFGWB #90-0067; 2/21/90). All 164-1 studies used Fortress 10G and exaggerated use rates. Almost all chlorethoxyfos remained in the top 3 inches of soil. The study authors calculated an initial dissipation half-life of 2.0 days for chlorethoxyfos in the top 3 inches of the Iowa loam soil and reported that 90% had dissipated in 17 days. For chlorethoxyfos in the top 3 inches of the Illinois clay loam soil, the study authors calculated an initial dissipation half-life of 2.6 days and reported that 90% had dissipated in 26 days. The fate of the degradates were not addressed.

MRID #41290605, (EFGWB #93-0258,-0259). Chlorethoxyfos dissipated with observed half-lives of 7-14 days in sandy loam soil in California and 14-35 days in clay loam soil in Iowa. In North Carolina, chlorethoxyfos dissipated with an observed half-life of 14-48 days from the upper 3 inches of a sandy loam soil and parent was detected into the 12- to 18-inch depth. Chlorethoxyfos leached into the 18- to 24-inch soil depth at the Iowa site, but did not leach below the 0- to 3-inch depth at the California site. The degradate trichloroacetic acid was detected at all sites, but the oxon analog of chlorethoxyfos, [IN-34158; phosphoric acid, diethyl (1,2,2,2-tetrachloroethyl) ester], was detected at the Iowa site (and Illinois) and did not leach below the 0- to 3-inch soil depth.

-Bioaccumulation in Fish (165-4); MRID #40883710, #41290621, EFGWB #90-186, 1/31/89, EFGWB #90-0067, 2/21/90. Channel catfish exposed to 0.0047 mg/L parent 1100 (muscle after 21 days), 4000 (viscera after 7 days), and 2100 (whole fish after 21 days exposure). BCF's after 28 days were 500 (muscle), 2000 (viscera), and 1100 (whole fish). After 14 days depuration, BCF's were greatly reduced 31 (muscle), 86 (viscera), and 46 (whole fish). Most of radioactivity (92-99%) in fish tissue and water was parent chlorethoxyfos.

Reserved:

-Photodegradation in Air (161-4); MRID #41736823, EFGWB #93-0258,-0259. Material balances were incomplete, and photodegradation on the glass surface could not be distinguished from the air, a new study is not currently required.

Supplemental:

-Field Volatility (163-3); MRID #43550307. At two separate sites in Oregon, MO (site 1), Bolckow, MO (site 2) chlorethoxyfos volatility was highest at Day 0 sampling time with measured concentrations of 1692.42 pg/liter and 68.71 pg/liter respectively. In general, a diurnal pattern of volatilization was observed with higher concentrations measured during nighttime and early morning sampling times. Half-lives calculated from field soil concentrations were 29 and 8 days at site 1 and 2 respectively.

11. COMPLETION OF ONE-LINER:

Attached.

12. CBI INDEX:

Not Applicable.

FORTRESS 2.5G



DuPont Agricultural Products

February 6, 1995

DuPont Agricultural Products
Registration & Regulatory Affairs
Walker's Mill, Barley Mill Plaza
P. O. Box 80038
Wilmington, DE 19880-0038
Fax: (302) 992-6470

Mr. Dennis H. Edwards, PM-19
Office Pesticide Programs
Registration Division (7505C)
Document Processing Desk
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20560-0001

Subject: DuPont Fortress® Granular Insecticide

**Application for Pesticide Registration of DuPont Fortress®
2.5G Granular Insecticide**

Dear Mr. Edwards:

We, the undersigned, E. I. duPont de Nemours and Company, hereby apply for registration of Fortress® 2.5G Granular Insecticide. An application for registration of Fortress® 5G Granular Insecticide (352-LLE), chlorethoxyfos, Fortress® Technical, (352-LLG) and a petition for tolerances of chlorethoxyfos on corn (3F4174) are all pending. Product chemistry and two toxicity studies (acute, oral LD50 for rat and acute, oral LD50 for bobwhite quail) conducted to support registration of Fortress® 2.5G are listed in this submission. All other data requirements for Fortress® 2.5G are being fulfilled by citing studies submitted to support the registration of Fortress® 5G and Fortress® technical (chlorethoxyfos). The tolerance petition, submitted in November, 1992, has been revised (request will be submitted in the beginning of February) to include sweet corn grain under field corn grain since the use patterns are similar. The proposed tolerances are:

<u>Commodity</u>		<u>ppm</u>
Corn, Field	Grain	0.01
	Forage	0.01
	Fodder	0.01
Corn, Pop	Fodder	0.01
	Grain	0.01
Corn, Sweet	Kernel and Cob with Husk Removed	0.01
	Forage	0.01
	Fodder	0.01

In support of the application for registration of Fortress® 2.5G Granular Insecticide, we respectfully submit the following:

- EPA Form 8570-1 (OPP ID No. 212510)
"Application for Pesticide Registration" of DuPont Fortress® 2.5G Granular Insecticide.
- EPA Form 8570-29
"Certification with Respect to Citation of Data" for DuPont Fortress® 2.5G Granular Insecticide.
- EPA Form 8570-10
"Label Technical Data" for DuPont Fortress® 2.5G Granular Insecticide.
- A Data Transmittal Document for new studies included in this application
- Releasable Summaries of Studies supporting this Application.
- A Data Matrix listing titles, MRID's, and submission dates of all studies supporting this application .
- EPA Form 8570-4
"Confidential Statement of Formula" for DuPont Fortress® 2.5G Granular Insecticide.
- Five (5) unbound copies of the proposed label for DuPont Fortress® 2.5G Granular Insecticide.
- Three (3) copies each of studies supporting the application.

This request for registration of a 2.5% granular formulation of Fortress® Insecticide contains three significant improvements over our previous submission for Fortress® 5G (5% granular formulation). The most obvious is the change in formulation strength of the granule from 5 to 2.5% which reduces the toxicity category from I to II and the label signal word from "Danger" to "Warning". DuPont intends to sell the 2.5% formulation in a bag for use by growers with conventional planters. Fortress® 5G will be sold only in the SmartBox™, a completely-enclosed, tamper-proof, delivery system for granular soil insecticides. These changes will

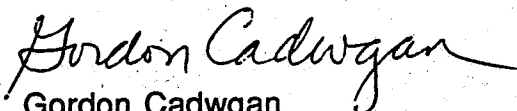
Mr. Dennis H. Edwards, PM-19
February 6, 1995
Page 3

significantly reduce worker exposure concerns. Second, the use rate for the 2.5G will be 6 oz. /1000 row feet and the use rate for the 5G will be reduced from 6 to 3 oz. /1000 row feet. This cuts in half the amount of active ingredient introduced into the environment and equally reduces any exposure concerns for avian, small mammals or aquatic species. Third, the concentration of active ingredient for Fortress 5G will be reduced to a nominal concentration of 5% (original submission was 5.45% nominal) and the 2.5G will be manufactured at 2.5% nominal. The net result of these three changes is significant reduction of the amount of insecticide needed to control corn rootworms and improved safety for growers and the environment.

Analytical and technical grade chlorethoxyfos have previously been submitted (December 14, 1990) to Mr. Harvey Hundley at the Analytical Chemistry Lab in Beltsville, MD. Analytical grade chlorethoxyfos and the oxon analog of chlorethoxyfos were also submitted (March 15, 1990) to Mr. Terry Bundy at the Pesticide and Industrial Chemicals Repository in Research Triangle Park, NC. When full scale production of Fortress® 5G and 2.5G begins at the end of 1995, we will submit the required 500-gram samples of each end product to Mr Hundley at the Analytical Lab in Beltsville, MD.

Please call me at (302) 992-6306 if you have any questions.

Sincerely,



Gordon Cadwgan
Product Registration Manager

GEC:smm

cc: Teung F. Chin - EPA

Fortress

Page _____ is not included in this copy.

Pages 14 through 20 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.
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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.

FORTRESS 5G

Fortress

Page ___ is not included in this copy.

Pages 22 through 27 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.
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ANAEROBIC AQUATIC METABOLISM DATA

Fortress

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Pages 29 through 32 are not included.

The material not included contains the following type of information:

- Identity of product inert ingredients.
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 - The document is not responsive to the request.
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DATA EVALUATION RECORD
DER 1

SHAUGHNESSY No. 129006
COMMON NAME: Chlorethoxyfos
CHEMICAL NAME: phosphorothioic acid, O,O-diethyl O-(1,2,2,2-tetrachloroethyl) ester]
FORMULATION: Fortress 5G
DATA REQUIREMENT: Field Volatility (163-3)

MRID No: 43550307

D. Larry Merricks, Michael P. Jensen. December 14, 1994.
Chlorethoxyfos Field Volatility Study. Performed by Agrisearch Incorporated 5734 Industry Lane Fredrick MD 21701. Sponsored by E.I. du Pont de Nemours and Company Dupont Agricultural Products Dupont Experimental Station Wilmington DE 19880-0402. Laboratory ID Agrisearch Project No. 1719, Dupont Protocol No. AMR 2315-92.

REVIEWED BY: Kevin L. Poff
Chemist EFGWB/EFED

Signature: *K. Poff*

Date:

APPROVED BY: Akiva Abramovitch, Ph.D.
Chemist EFGWB/EFED

Signature:

Date:

CONCLUSIONS:

1. Study MRID #43550307 is unacceptable and does not currently satisfy the field volatility (163-3) data requirement for chlorethoxyfos for the following reason:

a) The registrant is required to calculate the evaporate flux which would give a more practical rate of volatilization with respect to time as opposed to instantaneous measurements.

2. Study MRID #43550307 may be considered supplemental until the registrant submits the required calculations.

3. Following the application at two separate sites of Fortress 5G (chlorethoxyfos; [phosphorothioic acid, O,O-diethyl O-(1,2,2,2-tetra chloroethyl) ester] at the maximum use rate of 6 oz. formulation per 1000 ft. (6.7 lb formulated product/acre; 0.168 lb ai/Acre) row to a bareground plot by T-banding to a depth of approximately 1.5-2 inches using a 4 row corn planter the volatilization of chlorethoxyfos in **Oregon, MO** was at a maximum (Table XII; Low volume filters) of 1692.42 pg/liter (7:15 pm) on day 0 at the 15 cm sampling height, then decreased significantly through day 11 where a maximum of 70.82 pg/liter (1:10 pm) was measured at the 15 cm air sampler. On day 12 and 13 the measured air concentrations of chlorethoxyfos at 15 cm increased again to

153.61 pg/liter and 146.25 pg/liter. The amount of chlorethoxyfos found in soil core samples was at a maximum of 2.18 ppm on day 0 then decreased to 1.62 ppm by day 13; the calculated soil half-life of chlorethoxyfos was 29 days.

In Bolckow, MO, with an identical application as above, in May of 1992, the volatilization of chlorethoxyfos was at a maximum (Table XII; Low volume filters, 15cm) of 68.71 pg/liter on day 0 then decreased slowly to 6.44 pg/liter by day 10. Air concentrations then increased to 122.33 pg/liter on day 12, then decreased to 62.55 pg/liter on day 13. The amount of chlorethoxyfos found in the soil slab samples was at a maximum of 0.89 ppm on day 0 then decreased slowly to 0.29 ppm by day 13; the calculated soil half-life of chlorethoxyfos was 8 days.

MATERIALS AND METHODS:

Chlorethoxyfos [(phosphorothioic acid, O,O-diethyl O-(1,2,2,2-tetrachloroethyl) ester; Fortress, 98.4%, lot No. EH 953-0] was applied at the maximum use rate of 6 oz. formulation per 1000 ft. (6.7 lb acre) row to a bareground plot by T-banding to a depth of approximately 1.5-2 inches using a 4 row corn planter to two separate plots 200 ft. X 200 ft. containing 80 rows of application on April 17, 1992. The plot in Oregon MO was a silt loam (16% sand, 70% silt, 14% clay, 1.8% OM, pH 6.8, CEC (meq/100g) = 12.2; and the plot in Bolckow MO was a silt loam of higher organic matter (22% sand, 54% silt, 24% clay, 3.0% OM, pH 7.2, CEC (meq/100g) = 15.5).

To trap volatilized chlorethoxyfos air was drawn 570 L/minute through two 3.5 inch X 1 inch thick discs of polyurethane foam (prerinsed in acetone). Both discs were combined, heat sealed and immediately frozen. The high volume trap was mounted 5 ft. above the ground. A low volume air sampler had air drawn at 45 L/minute and consisted of a plastic PVC pipe (183 cm X 8.4 cm D) having four filter holders mounted at heights of 15, 40, 70 and 150 cm above the ground and which was centrally located. Sample collection began with the low volume collector at the top 150 cm and proceeded to the lower one at 15 cm.

During the first 3 days after application the low volume and high volume samplers were run for two hour intervals, four times during the day (starting approx. 1, 3, 5 and 8 hours after application) and once (two hour for the high volume and four hours for the low volume) during the night (approximately 12 hours after application). For the next 11 days, samplers were run for four hour intervals for the low volume and two hour intervals for the high volume twice during the day at 8:00 am and 2:00 pm and once during the night at approx. 8:00 pm.

Soil core samples were taken randomly from the test plots to determine soil moisture. (Site 1) Soil samples were taken before and soon after application and on days 8 and 13. Samples were not taken on days 2 and 5 due to rain. Fifteen soil core samples from within the application rows were taken at up to 6 inches; 5 7/8

inch cores were composited into a single replicate sample which was heat sealed and immediately frozen. Three replicates were obtained. (Site 2) Soil samples were taken before and immediately after application and on days 2, 5, 8, and 13. Three soil slab samples (9 inch length X 1 inch width to a depth of 4 inches) each representing a replicate sample were heat sealed and immediately stored frozen. All samples were shipped to Agrisearch on dry ice overnight.

Analytical grade compound was used to field spike the low and high volume filters at 1 mg/ml.

RESULTS:

Site 1 (Oregon, MO; Holt County)

Following the application of Fortress 5G (chlorethoxyfos; [phosphorothioic acid, O,O-diethyl O-(1,2,2,2-tetra chloroethyl) ester] at the maximum use rate of 6 oz. formulation per 1000 ft. (6.7 lb formulated product acre; 0.168 lb ai/Acre) row to a bareground plot by T-banding to a depth of approximately 1.5-2 inches using a 4 row corn planter in April 1992, the volatilization of chlorethoxyfos was at a maximum (Table XII; Low volume filters) of 1692.42 pg/liter (7:15 pm) on day 0 at the 15 cm sampling height, then decreased significantly through day 11 where a maximum of 70.82 pg/liter (1:10 pm) was measured at the 15 cm air sampler. On day 12 and 13 the measured air concentrations of chlorethoxyfos at 15 cm increased again to 153.61 pg/liter and 146.25 pg/liter. The amount of chlorethoxyfos found in soil core samples was at a maximum of 2.18 ppm on day 0 then decreased to 1.62 ppm by day 13; the calculated soil half-life of chlorethoxyfos was 29 days.

During the 14-day study period, little precipitation occurred, air temperatures ranged from 8.8 to 38.1 C, total daily solar radiation ranged from 15 to 1410 kWatts/m², maximum wind gusts were present during daytime hours and reached up to 28 MPH at the 70 cm height. Soil temperatures at 5 mm ranged from 1 to 27 C. Relative humidity ranged between 29 and 86%. During the study, the soil moisture content increased from an average of 17.2% on day 0 to 20.78% by day 8, then decreasing to 16.57 by day 13.

Site 2 (Bolckow, MO; Andrew County)

Following the application of Fortress 5G (chlorethoxyfos; [phosphorothioic acid, O,O-diethyl O-(1,2,2,2-tetra chloroethyl) ester] at the maximum use rate of 6 oz. formulation per 1000 ft. (6.7 lb acre) row to a bareground plot by T-banding to a depth of approximately 1.5-2 inches using a 4 row corn planter in May of 1992, the volatilization of chlorethoxyfos was at a maximum (Table XII; Low volume filters) of 68.71 pg/liter on day 0 then decreased slowly to 6.44 pg/liter by day 10. Air concentrations then increased to 122.33 pg/liter on day 12, then decreased to 62.55 pg/liter on day 13. The amount of chlorethoxyfos found in the soil slab samples was at a maximum of 0.89 ppm on day 0 then decreased slowly to 0.29 ppm by day 13; the calculated soil half-life of

chlorethoxyfos was 8 days.

During the 14-day study period, little precipitation occurred, air temperatures ranged from 4.9 to 35.2 C, total daily soil radiation ranged from 15 to 1290 kWatts/m² maximum wind gusts were present during daytime hours and reached 30.6 MPH at 150 cm. Soil temperatures at 5 mm ranged from 8 to 24 C. Relative humidity ranged between 32 and 85%. During the study, the soil moisture content remained relatively constant at 16 to 17%.

DISCUSSION:

1. The study authors suggests that relative humidity increases chlorethoxyfos soil volatility more than does temperature since relative humidity increases and temperature decreases for night time and early morning sampling, also a rain event at site 2 late in the study stimulated an increase in chlorethoxyfos volatilization which further supports that affirmation.

The EFGWB believes that more important to the relative humidity in the volatilization of chlorethoxyfos was the wind velocity. The measured concentrations of the vapor density were higher during the samples taken in early morning than the mid morning-day cycle. One would expect the flux (quantity volatilizing from soil to air) of chlorethoxyfos to be higher during the day cycle due mainly to the higher ambient air and soil temperatures. However, this study indicates the contrary is true, mainly due to the small increase in wind velocity during the day hours which increases the vapor dispersion lowering measurable concentrations of chlorethoxyfos and possibly the rate of volatilization of chlorethoxyfos from the soil as well. The rain event in the second week at Site 2 increasing chlorethoxyfos volatilization was more than likely a result of residual compound in the dissolved granular being driven off due to a high Henry's law constant (1.5×10^{-2} , 3.5×10^{-4} atm m³ mole⁻¹) and the volatile nature of the compound. Dryer conditions would form a crust on the soil surface decreasing volatilization rates, however other studies would be required to determine the overall and individual effects of the wind velocity (convection, advection), relative humidity, and soil temperatures.

2. There was no statistical analysis completed on the data. Only means, linear regressions and sums were used. The registrant is required to calculate the evaporative flux using a gradient method utilizing the vertical gradient measurements of horizontal wind speed, air temperature and pesticide concentrations. There is a modified equation where there is compensations for conditions which cause the atmosphere to be stable or unstable. The method is a modified form of the Thornthwaite-Holzman equation (Majewski, M.S., M.M. McChesney, J.N. Seiber, 1991; A field comparison of two methods for measuring DCPA soil evaporation rates, Environmental Toxicology and Chemistry 10: 301-311.), which is based upon the log law of the wind speed profile.

3. The site history was not described. Previous pesticide applications to the site were not reported. The abstract,

discussion and results talked little of actual quantitative data gained from completing the study.

4. The longest period that field samples (foam filters) were stored prior to analysis was 139 days. Length of storage to analysis of field soil samples was not discussed, nor was storage stability of residues on soil.

5. A comparison of the two half-lives generated from the two separate field studies is not valid due to two different methodologies used in collecting field soil samples. At site 1 soil cores were the choice of sampling and at site 2 a soil "slab" was collected.

6. Snow and rain at Site 1 caused study delays due to wet conditions. Sampling was not performed on days 3 and 4 (Table II and V). Sampling was not performed on day 11 at Site 2 due to a rain event.

7. The GC analytical method limit of detection was determined to be 2.5 pg/4 ul injection (2X instrumental background noise) and the quantitation limit 2X the detection limit. For 1 foam filter the quantitation limit was 0.250 ug for 2 foam filters it was 0.438 ug and for soil it was 0.125 ppm (dry weight).

8. Laboratory studies indicated that there was no appreciable breakthrough of chlorethoxyfos from the polyurethane filters in the low and high volume sampling pumps. Storage stability indicated chlorethoxyfos did not degrade on the polyurethane foam under freezer conditions and also that the compound was stable through freezing, freezer storage, shipment or field handling.

9. The registrant reported that Fortress 5G chlorethoxyfos is being developed for on field corn during planting time applications for the control of corn rootworm, cutworm, wireworm, white grubs, and seed corn maggot. The maximum application rate is 6.7 lb of formulated product per acre.

Fortress

Page _____ is not included in this copy.

Pages 37 through 67 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.

Environmental Fate & Effects Division
 PESTICIDE ENVIRONMENTAL FATE ONE LINE SUMMARY

CHLORETHOXYFOS

Last Update on June 29, 1995

[V] = Validated Study [S] = Supplemental Study [U] = -USDA Data

LOGOUT	Reviewer:	Section Head:	Date:
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Common Name: CHLORETHOXYFOS

Smiles Code:

PC Code # :129006

CAS #:54593-83-8

Caswell #:

Chem. Name :phosphorothiotic acid, O,O-diethyl O-(1,2,2,2-tetrachloro ethyl) ester

Action Type:Soil insecticide;controls corn rootworm and other soil pests

Trade Names:Fortress

(Formul'tn):Granular 2.5G and 5G

Physical State: liquid

Use :Terrestrial Food uses

Patterns :proposed use rate is 0.3oz ai/1000 ft row = 0.25 lb/ai/acre

(% Usage) :

Empirical Form: $C_6H_{11}Cl_4O_3PS$

Molecular Wgt.: 336.00

Vapor Pressure: 1.70E -3 Torr

Melting Point : °C

Boiling Point: 105 .8toff

Log Kow : 4.59

pKa: @ °C

Henry's : 3.50E -4 Atm. M3/Mol (Measured)

3.58E -4 (calc'd)

Solubility in ...

Comments

Water	2.10E	ppm	@25.0	°C
Acetone	E	ppm	@	°C
Acetonitrile	E	ppm	@	°C
Benzene	E	ppm	@	°C
Chloroform	E	ppm	@	°C
Ethanol	E	ppm	@	°C
Methanol	E	ppm	@	°C
Toluene	E	ppm	@	°C
Xylene	E	ppm	@	°C

Hydrolysis (161-1)

[V] pH 5.0:72 days,chloral hydrate major degradate.

[V] pH 7.0:59 days,chloral hydrate major degradate.

[V] pH 9.0:4.3 days,dichloroacetic acid major degradate.

[] pH :

[] pH :

[] pH :

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Photolysis (161-2, -3, -4)

[V] Water: 27 days (uncorrected for light intensity or continuous rad.
[] : @ pH 5 Xenon light, chloral hydrate and DCA major deg.
[] : Dark control half-life was 89 days, corresponding to hydro.
[] :

[V] Soil : 21 days nat. sun. chloral hydrate, polars, CO₂ degradates.
[] Air :

Aerobic Soil Metabolism (162-1)

[V] 20 day half-life in a static system. Major degradates were CO₂
[] chloral hydrate.
[] In a flow through system, half-life was 7 days. Volatilization
[] contributed most to dissipation. Some chloral hydrate and CO₂
[] was detected.
[]
[]

Anaerobic Soil Metabolism (162-2)

[V] Half-life was 41-47 days in clay soil. Only chlorethoxyphos
[] was identified in the soil and floodwater. CO₂ was the major
[] degradate totalling 36.5% at 62 days incubation.
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Anaerobic Aquatic Metabolism (162-3)

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Aerobic Aquatic Metabolism (162-4)

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Soil Partition Coefficient (Kd) (163-1)

[V]	Soil	OM%	Kdads	Kddes
[]	Hanford SdLm	1.0	40	7.5
[]	North Car.LmSd	2.0	53	8.2
[]	Fargo StLm	4.3	150	5.3
[]	LaHogue Lm	5.0	200	5.2
[]	Parent binds strongly to soil.			

Soil Rf Factors (163-1)

[V] Adsorption desorption literature indicate that chloral hydrate
[] and trichloroacetic acid have Kd values of 0.1 to 0.3.
[] Soil column leaching studies indicate that chloral hydrate
[] is easily leached from four test soils indicating high mobility
[] of degradates.
[]

Laboratory Volatility (163-2)

[V] Mass flux was measured at 45.6 sq.cm. Rate of volatilization
[] was inversely proportional to soil OM

Field Volatility (163-3)

[S] Highest conc. meas. at day 0 at 15 cm height, @ 1692.42 pg/L
[] soil t1/2=29 and 8 days at 2 separ. sites.

Terrestrial Field Dissipation (164-1)

[V] Half-life of 2.0 days in the top 3 inches in Iowa
[V] Half-life of 2.6 days in Illinois
[V] Half-life of 14-35 days in Illinois
[V] Half-life of 14-48 days in North Carolina in top 3 inches.
[V] Half-life of 7-14 days in California.
[] Parent was detected in the 12 to 18 inch depth in N.C.
[] Parent was detected in the 18 to 24 inch depth in Iowa
[] Parent did not leach below 3 inches in CA
[] The oxon analog was detected in Illinois and Iowa, the major
[] degradate detected in all sites was trichloroacetic acid.

Aquatic Dissipation (164-2)

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[]
[]
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[]

Forestry Dissipation (164-3)

[]
[]

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Long-Term Soil Dissipation (164-5)

[]
[]

Accumulation in Rotational Crops, Confined (165-1)

[]
[]

Accumulation in Rotational Crops, Field (165-2)

[]
[]

Accumulation in Irrigated Crops (165-3)

[]
[]

Bioaccumulation in Fish (165-4)

[V] Channel Cat. exposed to 0.0047 mg/L parent showed BCF's 1100 mus.
[] 4000 vis., 2100 whole fish; 2wks depuration gave 31, 86,46 resp.

Bioaccumulation in Non-Target Organisms (165-5)

[]
[]

Ground Water Monitoring, Prospective (166-1)

[]
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[]
[]

Ground Water Monitoring, Small Scale Retrospective (166-2)

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[]

Ground Water Monitoring, Large Scale Retrospective (166-3)

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Ground Water Monitoring, Miscellaneous Data (158.75)

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[]
[]

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Field Runoff (167-1)

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Surface Water Monitoring (167-2)

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[]

Spray Drift, Droplet Spectrum (201-1)

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[]

Spray Drift, Field Evaluation (202-1)

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[]
[]

Degradation Products

Dichloroacetic acid abiotic hydrolysis pH 7-9
Chloral hydrate abiotic hydrolysis pH 5-7
CO2 aerobic/anaerobic soil
Trichloroacetic acid aerobic soil and plant; found in terr. field.
Oxon analog; phosphoric acid, diethyl (1,2,2,2-tetrachlorethyoxyph.
was detected in the field at Iowa and Illinois.
Based upon literature review, DETP diethylthiophosphate and DEP
diethylphosphate are the major degradates of the phosphoryl moiety.

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Comments

TCA was detected in the terrestrial field dissipation studies and is considered to be highly mobile. It is unclear if TCA can be metabolized microbially.

References: EFGWB#93-0258-0259
Writer : KLP