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ENVIRONMENTAL FATE AND GROUND WATER BRANCH

Review Action

To:

Susan Lewis, PM #03

Special Review and Reregistration Division (H7508W)

From:

Kevin Poff, Chemist

Environmental Fate & Monitoring Branch/EFED (H7507C)

Thru:

Betsy Behl, Chief

Environmental Fate & Monitoring Branch/EFED (H7507C)

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Attached, please find the EFGWB review of...

Common Name:	Chlorethoxyfos Trade name: Fortress
Company Name:	E.I. Dupont de Nemours and Co., Inc.
ID #:	000352-0053
Purpose:	To review additional data submitted to upgrade a previously reviewed Field Volatility (163-3) study.

Type Product:	Action Code:	EFGWB #(s):		Review Time:
Insecticide	570		 -	5.0 days

STATUS OF STUDIES IN THIS PACKAGE:

Guideline MRID Status 163-3 44361301 A

STATUS OF DATA REQUIREMENTS ADDRESSED IN THIS PACKAGE:

Guideline #	Status
#	
163-3	S
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2Study Status Codes: A=Acceptable U=Upgradeable C=Ancillary I=Invalid.
Data Requirement Status Codes: S=Satisfied P=Partially satisfied N=Not satisfied R=Reserved
W=Waived.

1. CHEMICAL:

Common Name: Chlorethoxyfos

Trade Name: Fortress

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

Chemical Name: phosphorothioic acid, 0,0-diethyl 0-(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 X 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)

U.V. max. = <290 nm

2. TEST MATERIAL:

See attached DER.

3. STUDY/ACTION TYPE:

To review supplemental data submitted to upgrade a previously reviewed Field Volatility (163-1) study to acceptable status.

4. STUDY IDENTIFICATION:

(Original study) MRID No: 43550307 D. Larry Merricks, Michael P. Jensen. December 14, Chlorethoxyfos Field Volatility Study. Performed by Agrisearch Incorporated 5734 Industry Lane Frederick 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.

(Supplemental Information) MRID No: 44361301 Aldos Barefoot. August 20, 1997. Chlorethoxyfos Field Volatility Study. Sponsor: E.I. du Pont de Nemours and Company, Wilmington DE Laboratory Project ID, Dupont Report No. AMR 2315-92, Agrisearch Project No. 1719[AMR 2315-92].

5. REVIEWED BY:

Kevin L. Poff, Chemist Fate and Monitoring Branch Environmental Fate and Effects Division

Date: 10/8/47

6. APPROVED BY:

Betsy Behl, Branch Chief Fate and Monitoring Branch Environmental Fate and Effects Division Wy Bell Date: 10/9/97

7. <u>CONCLUSIONS</u>:

Field Volatility (163-3): MRID's #43550307 and #44361301

1. Together studies MRID #43550307 and #44361301 completely satisfy the Field Volatility (163-3) data requirement for chlorethoxyfos.

2. Following the application at two separate sites of Fortress 5G (chlorethoxyfos; [phosphorothioic acid, 0,0-diethyl 0-(1,2,2,2-tetra chloroethyl) ester] at the maximum use rate of 6 oz. formulation per 1000 ft. row (6.7 lb formulated product/acre; 0.168 lb ai/Acre) 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, MT 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.

Conclusions: (Supplemental data, MRID #44361301)

Results of the study indicate that chlorethoxyfos volatilization accounted for approximately 10% of the total mass lost through dissipation. The evaporative flux in Oregon reached a maximum of 290 ug/m²-hr on the second day of the study and decreased to negligible levels by the third day (7 ug/m²-hr.). The flux remained below 10 ug/m²-hr from day 2 through day 11 and increased to about 20 ug/m²-hr on the last two days of the study. The study authors attributed the volatilization to the cooler wetter environmental conditions. The soil was a silt loam soil with 1.8% organic matter.

In Bolckow, MT, 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

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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. Conclusions: (Supplemental data, MRID #44361301)

The results of the study indicate that less than 0.5% of the total applied mass of chlorethoxyfos was lost through volatilization. The evaporative fluxes calculated for the Montana site never exceeded 5 ug/m^2 -hr. The study authors attributed the lack of volatilization to the adsorption of chlorethoxyfos to the soil and a dry soil surface during many sampling periods. The soil was a silt loam with 24% clay and 3.0% organic matter.

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. Freundlich adsorption coefficients in soils of varying organic matter content ranged from K_{ads} 40 to 200, terrestrial field half-lives ranged from 2 to 2.6 days and half-lives calculated from field soil concentrations in the field volatility studies were 8 and 29 days. Dissipation in soil is through microbial processes yielding trichloracetaldehyde then CO₂.

Soil conditions seem to strongly affect the volatilization of the compound. The higher percentage of organic matter, and clay content lowers the rate of volatilization. The field volatilization study conducted in Oregon, Montana with a silt loam soil (16% sand, 70% silt, 14% clay, 1.8% OM, pH 6.8, CEC meq/100g = 12.2) showed a greater volatilization rate (approx. 10% of applied) than the Bolckow, Montana silt loam site (approx. 0.5% of applied) that had a higher associated clay and organic matter content (22% sand, 54% silt, 24% clay, 3.0% OM, pH 7.2, CEC meq/100g = 15.5). 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 probably 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 X 10⁻², 3.5 X 10⁻⁴ atm m³ mole⁻¹).

8. <u>RECOMMENDATIONS</u>:

Inform the registrant that the field volatility (163-3) data requirement is fully satisfied for chlorethoxyfos.

9. 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, and also causes depression of cholinesterase.

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. Fortress 10G was formulated specifically for these field studies and is not a new product to be registered.

This review addresses the deficiencies noted in a previously reviewed field volatility (163-1) dated 7/13/95. The registrant

was required to calculate the evaporate flux of chlorethoxyfos which would give a more practical rate of volatilization with respect to time as opposed to instantaneous measurements.

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

Satisfied:

120 days posttreatment.

-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

-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.

<u>Leaching/Adsorption/Desorption</u> (163-1); MRID #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 The Freundlich binding coefficients and organic matter soils. 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 indicate 1/n = 0.12. These results that 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.

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

-<u>Field Volatility</u> (163-3); MRID #43550307. At two separate sites in Oregon, MT (site 1), Bolckow, MT (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 field Half-lives calculated from times. concentrations were 29 and 8 days at site 1 and 2 respectively. At site 1 the contribution of volatilization to the total loss of applied mass of chlorethoxyfos was 10%; at site 2 the contribution was 0.5%. At site 1 the evaporative flux reached a maximum of 290 ug/m² -hr on the second day of the study and decreased to negligible levels by the third day (7 ug/m² -hr.). The flux remained below 10 ug/m² -hr from day 2 through day 11 and increased to about 20 ug/m² -hr on the last two days of the study. At site 2 the evaporative flux never exceeded 5 ug/m² -hr. authors attributed the lack of volatilization to the adsorption of chlorethoxyfos to the soil and a dry soil surface during many sampling periods.

-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 <u>Iowa</u> loam soil and reported that 90% had dissipated in 17 days. For chlorethoxyfos in the top 3 inches of the <u>Illinois</u> 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.

<u>Reserved/supplemental</u>:

-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.

- 10. <u>DISCUSSION</u>: See attached DER.
- 11. <u>COMPLETION OF ONE-LINER</u>: Attached.
- 12. <u>CBI INDEX</u>: Not Applicable.