DATA EVALUATION RECORD
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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 (Initial Study)
D. Larry Merricks, Michael P. Jensen.   December 14, 1994. 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.

MRID No: 44361301 (Supplemental Data)
Aldos Barefoot. August 20, 1997. Chlorethoxyfos Field Volatility Study. Sponsor: E.I. du Pont de Nemours and Company, Wilmington DE 19898. Laboratory Project ID, Dupont Report No. AMR 2315-92, Agrisearch Project No. 1719 [AMR 2315-92].

REVIEWED BY: Kevin L. Poff/Chemist   Signature: _____
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CONCLUSIONS:

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, 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, 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

1

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.

Conclusion: (MRID #44361301)

Results of the study indicate that chlorethoxyfos volatilization accounted for approximately 10% of the total mass lost through dissipation. The evaporative flux calculated from data in Oregon reached a maximum of 290 ug/m^2 -hr on the second day of the study and decreased to negligible levels by the third day (7 ug/m^2 -hr.). The flux remained below 10 ug/m^2 -hr from day 2 through day 11 and increased to about 20 ug/m^2 -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 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.

Conclusion: (MRID #44361301)

The results of the study indicate that less than 0.5% of the total applied mass of chlorethoxyfos was loss 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 a heavier clay and organic matter content 24% and 3.0% respectively.

MATERIALS AND METHODS: (MRID #43550307)

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 MT 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 MT 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. The sampler was centrally located. Sample (filter removal) 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, MT;Holt County) (MRID #43550307)

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.

3

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/m^2, 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, MT;Andrew County) (MRID #43550307)

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/m^2 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%.

Supplemental Information (MRID #44361301)

Methods:

Test plot details and application procedures are outlined above. Wind speeds at four heights 20, 40, 70 and 150 cm were measured by four rotating cup anemometers. High volume and low volume samplers were used. Thermocouples located at 30 and 80 cm heights measured the temperature gradient and defined the average temperature at 50 cm. Solar irradiance, barometric pressure, soil temperature, wind direction and relative humidity were measured as described above. Meteorological data were taken every 5 minutes during the sampling period.

Methods were developed to allow quantitation of chlorethoxyfos in air samples at an LOQ of 0.25 ug/filter. The typical air sampling flow rate was about 45 liter/min, giving total sample volumes of 5.4 m^3 and 10.8 m^3 for 2 and 4 hour samples respectively which related to a limit of quantitation of approximately 0.05 ug/m^3 or 0.025 ug/m^3.

4

<u>Calculations</u>:

The evaporative flux ug/m^2 -hr for each sampling time period was calculated using equation 1 (see appendix 1 for sample calculation). Empirical correction factors were included in the equation to account for diabiatic or non-ideal conditions. Concentration and wind speed gradients were obtained from regression equations fit to the experimental data during each sample period. The regression equations were then used to calculate wind speeds and concentrations at 80 and 30 cm. Total mass volatilized during each sampling period was calculated as the product of the evaporative flux, sampling time, and site area. The flux during non-sampling intervals was estimated from measurements made under similar conditions or adjacent sampling periods.

<u>Results</u>:

The concentration of chlorethoxyfos in air was usually log-linear with height at both sites (Tables 5 and 6). At site 2 the concentrations were often below the limit of quantitation, and the concentration gradients for many samples reflect higher errors than for results greater than the LOQ. Figure 4a shows a non-linear concentration gradient as chlorethoxyfos was not detected above 15 cm. This would result in a large error in calculating the flux however the very low concentrations measured indicate that the flux would be low and the total mass loss to volatilization would also be low.

The concentration of chlorethoxyfos in air samples from Site 1 decreased dramatically when heavy rain saturated the soil (after day 1 samples). Air concentrations remained low (<0.1 ug/m^3) until the last two days of the study when the soil began to dry. The air concentrations on days 12 and 13 were approximately 10% of those observed on days 0 and 1. At site 2 the air concentrations were less than 0.1 ug/m^3 at all sampling heights except the day 12, 15 cm sample when chlorethoxyfos concentration was 0.12 ug/m^3.

In general the evaporative fluxes calculated from Site 2 were much lower than for Site 1 and never exceeded 5 ug/m^2 -hr during the duration of the study. The shallow wind speed gradients and low air concentrations were the deciding factors in the calculation of evaporative flux. Volatilization was initially inhibited at Site 1 by water saturated soil and snow but increased as the soil dried and temperature increased. At Site 2 volatilization was reduced by the dry soil surface, adsorption of chlorethoxyfos to soil organic matter, and shallow wind speed gradients. From the estimated and measured fluxes, time periods and area of the treated plot, the mass of chlorethoxyfos that was volatilized each day was calculated (Tables 7 and 8). In Figure 9, the chlorethoxyfos volatilization during sampling and non-sampling periods is shown. At Site 1, the mass of chlorethoxyfos volatilized accounted for approximately 9% of the application and 33% of the chlorethoxyfos lost to

degradation (Table 10). At Site 2, volatilization accounted for about 0.4% of the application and 68% of the chlorethoxyfos degraded.

When winds were calm or when there was no difference between the wind speed or concentration at 30 and 80 cm (Site 2 days 3,4,9,15,16,17,18,23,26,39) fluxes were assumed to be zero. The expected influence of solar irradiance on atmospheric stability is apparent from plots of the change in temperature and irradiance for Site 2 (Figure 7). The sampling schedule at Site 2 included several night samples during which the air was stable inhibiting volatilization and fluxes were small. Stable and neutral air were observed at night and in early morning and late afternoon. As the solar irradiance increased during the day warming the soil surface the change in temperature was negative (delta T). Although the unstable air increased the calculated flux, the fluxes were small and indicate factors other than the atmospheric stability controlled volatilization.

DISCUSSION:

1. The study authors used the aerodynamic (AD) profile method to calculate the evaporative flux of chlorethoxyfos under varying corn growing conditions to determine the contribution of volatilization to dissipation. Wind speed gradients, temperature and concentration gradients are used in the calculation that assumes a steady state condition which produces a boundary layer over the experimental site.

2. The study authors state that the mathematical expression for the evaporative flux using the method assumes steady state conditions which produce a boundary layer over the experimental site. The treated area must be large enough so that the upwind fetch is about 100 X the sampling height. The conditions for which the model is appropriate result in wind speeds that increases with height in a logarithmic progression and concentrations that decrease. Deviations from these ideal conditions typically result in underestimates of the evaporative flux.

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