DATA EVALUATION RECORD

STUDY 10

CHEM 036101  Trifluralin  §163-3

FORMULATION--12--EMULSIFIEABLE CONCENTRATE (EC)

STUDY ID 40673601E

DIRECT REVIEW TIME = 10

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CONCLUSIONS:

Mobility - Field Volatility

This field volatility study provides supplemental data. It cannot be used to fulfill the data requirement (163-2). These data were taken from published articles and were not originally designed to satisfy Subdivision N data requirements. Therefore, it is difficult to draw the conclusions needed for an environmental fate assessment. However, these data and the other published volatility data submitted (MRID 40673601A, 40673601B, 40673601C, 40673601D, 40673601F, 40673601G) do indicate the following:

1. Volatility may be a major route of dissipation for trifluralin.
2. Trifluralin appears to volatilize (≈25 to 60% of applied in 11 days).

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3. Laboratory volatility data are needed to determine relative rate of dissipation due to volatility in relation to other routes of dissipation.

4. No further field volatility data are needed until evaluation of acceptable laboratory volatility data is completed.

In this study the soil was not analyzed for trifluralin. Therefore, the application rate was not confirmed, and the concentration of trifluralin in the air could not be related to the concentration of trifluralin in the soil.

METHODOLOGY:

Trifluralin (44.5% EC) was surface applied as a spray to sandy loam soil (63.9% sand, 23.6% silt, 12.5% clay, 0.55% organic carbon, pH 6.5, CEC not provided) in an experimental watershed (1.26 ha) located in Georgia, at 1.17 kg/ha, in June 1973. The trifluralin was incorporated to 7.5 cm and the plot was planted to soybeans. After planting, a sampling system consisting of two masts with three samplers/mast at 20, 80, and 160 cm above the soil surface was established. The samplers were connected to a vacuum pump and air (6 L/minute) was drawn through an ethylene glycol trapping solution; the tubing and trap were wrapped in aluminum foil to prevent photolysis. During the study, air samples (3- or 4-hour collection time) were collected at 0-2, 17, and 34 days (June 15-17, June 20, July 2, and July 19). Soil samples were collected "hourly" with a spatula or soil corer at various increments to a depth of 15 cm and analyzed for soil moisture.

Trifluralin was extracted from the ethylene glycol in the traps by shaking with benzene; the benzene extract was analyzed by GC with electron capture detection. Trapping efficiency of trifluralin was 90%; the recovery efficiency of trifluralin from ethylene glycol traps was 90%.

Wind speeds, air and soil temperatures, atmospheric water vapor pressure, net radiation, and soil heat flux were measured intensively over the plot.

DATA SUMMARY:

Trifluralin (44.5% EC) volatilized from sandy loam soil that was treated at 1.17 g/ha in June, 1973; the maximum air concentration of trifluralin was 3403 ng/m³ on the day of application. The pesticide flux ranged from 1 to 40 g/ha/day (reviewer approximated from Figures 3-6) on the four days samples were taken. Cumulative losses were not calculated.

The slope of the test plot was 3.0%
COMMENTS:

1. Soil samples were not analyzed for trifluralin. Therefore, the pattern of decline of trifluralin from the soil could not be measured. In addition, the application rate was not confirmed, and the concentration of trifluralin in the air could not be related to the amount of trifluralin in the soil.

2. The study authors stated that the pesticide flux ceased when the soil water content was less than three molecular layers of water. Soil adsorption of trifluralin was apparently reversible since an increase in the water content above three molecular layers caused a greater pesticide flux. In general, pesticide flux was lower during the day when evaporative demand was high, and flux increased at night when the soil was rewetted from upward water movement. If the soil is wet, flux is influenced by turbulence and temperature.

3. This study was published and not intended to fulfill Subdivision N guidelines. Most of the information provided is not relevant to Subdivision N guidelines.

4. Volatility was expressed as g/ha/day and air concentrations as ng/m³. All data were presented as figures, which did not allow the reviewer to assess variability. The figures and minimal tabular data provided were barely legible in the copy provided for review. No specific data could be cited from the figures.

5. An adsorption K value and CEC were not provided for the soil used in these experiments.

6. Wind speed, air temperature, soil temperature, and radiation were reported in graphic form for sampling days. Weather information, including precipitation and irrigation data, was not provided for the study period.

7. EFWB prefers that [14C]residues in samples be separated by chromatographic methods (such as TLC, HPLC, and GC) solvent systems of different polarity, and that specific compounds isolated by chromatography be identified using a confirmatory method such as MS in addition to comparison to the Rf of reference standards. In this study aliquots of the extracts were analyzed by GC.

8. The study authors cite Spencer and Cliath (Study 7, MRID 40673601B) for the vapor density measurements of trifluralin as 4.26 x 10⁶ ng/m³ at 30 C.

9. A second study was also discussed in this paper. Since this second study was mainly concerned with photodegradation and volatilization of trifluralin compared to lindane, and no quantitative data were reported, this study was not discussed in this review.

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10. This study is one of several published papers included as appendices to MRID 40673601 (Day, E.W. 1988. Laboratory and field volatility studies with trifluralin from soil. Laboratory Project ID. EWD8807). This document was submitted as an assessment of the potential inhalation hazard of trifluralin to exposed workers. Because this portion of the document contains summary data only and is not pertinent to Subdivision N guidelines, it was not reviewed; only the published papers in the appendices have been reviewed.
STUDY AUTHOR(S)'S RESULTS AND/OR CONCLUSIONS

(INCLUDING PERTINENT TABLES AND FIGURES)
The energy balance method is useful for calculating fluxes during light periods. Large relative errors which occur in the (3rd/2nd) and (3rd/3rd) terms (Fig. 1) in early morning and late afternoon, and in nighttime periods when radiation approaches the opposite value of soil heat flux, make this method impractical during these periods. The momentum balance method is valid theoretically only during adiabatic conditions which prevail only briefly in the early morning and late afternoon.

Stability corrections must be applied to correct the transfer coefficients for all conditions of thermal stability. Despite these efforts, it is clear that the energy balance method is the most practical approach for the simultaneous determination of the momentum and latent heat fluxes. Further, the assumption of adiabatic conditions is valid only when the height of the canopy is less than 2 meters.

The momentum balance method is used to calculate water vapor (E) and temperature (T) fluxes from the top of the canopy. The momentum balance equation is given by:

\[ E = C_e \frac{d}{d} \]

where \( E \) is the water vapor flux, \( C_e \) is the aerodynamic resistance coefficient, and \( \frac{d}{d} \) is the surface resistance coefficient. The surface resistance is determined by the ability of the soil surface to release water vapor to the atmosphere.

The water vapor flux is calculated by substituting the values of the surface resistance and aerodynamic resistance into the momentum balance equation. The results are expressed in terms of the water vapor flux per unit area and unit time.

The surface temperature is measured with thermocouples at depths of 0.01, 0.02, and 0.03 m. Soil samples are taken at sampling locations at depth intervals of 0.01, 0.02, and 0.03 m, and 0.04 to 0.06 m. The samples are composited and analyzed for soil properties. The samples are then compared to determine the extent of water content determined gravimetrically.

On June 18 an irrigation system was applied to the experimental field. The irrigation system was designed to provide a uniform distribution of water over the field. The irrigation system was designed to provide a uniform distribution of water over the field. The irrigation system was designed to provide a uniform distribution of water over the field. The irrigation system was designed to provide a uniform distribution of water over the field.
rapid volatilization is reflected in the high average fluxes during the 1000 to 1400-hour sample event, though soil water content was increased only during the last 30 min of the sampling period. After the rainfall, fluxes responded to other factors in addition to soil water content. It seemed to be affected primarily by turbulence (Ks, Fig. 5B) and to a lesser extent, by soil temperature (Fig. 5D). Atmospheric stability (Fig. 5A) seemed to have little influence on the overall pesticide concentrations. Except during the early morning dry period and late evening, when the flux dropped slightly while the concentrations remained rather constant.

Late in the season (September 15) data were collected after a rain on an overcast, rather cold day with adequate water availability. There was little change in any soil or microclimatic parameters (Fig. 5A, C, and D) and little change in pesticide volatilization or air concentrations throughout the day (Fig. 6A and B).

It is obvious that rain and low temperatures control volatilization. Air and soil temperatures were only a small fraction of air saturation equilibrium values (4.25 x 10^4 ng/m^3 at 30°C [Spencer and Clasie, 1974]). The highest observed value at 20 cm after application and incorporation was 3.013 ng/m^3 with an air temperature of 25°C on 15 June 1973 (White et al., 1976). Spencer and Clasie (1974) passively through Gila soil, and reported an equilibrium vapor density of approximately 0.2 x 10^9 ng/m^3 for similar soil concentrations and soil water content (1.85 mg/g and 6.0% water, respectively) to our highest flux situation. Our highest air concentration of 3.013 ng/m^3 represents approximately 3% of the vapor density corresponding to equilibrium between the atmosphere and soil surficial at the soil surface. It is evident that diffusion into air is not rate limiting and rapid dispersal was occurring. Furthermore, residence times within the 20- to 160-cm volume of soil (pesticide concentration present in a volume of air divided by the pesticide flux through it) showed rapid dispersal of pesticide after it left the soil surface. During the first 2 measurement days (15-16, 20 June and 2 July), when there was little canopy development, the residence times ranged from 20 to 40 sec during the periods of highest turbulent transfer conditions (1000 to 1700 EDT) to 2 min during the more stable periods of the early morning hours (2400 to 0600 EDT). On 15 July, the residence time for the layer between 80 and 160 cm (canopy height was 40 cm) ranged from 10 to 30 sec. As evidenced by the concentration gradients in Fig. 5A, 4A, 5A, and 6A, there was always a rapid dispersal of volatilized surficial from the soil during atmospheric stable conditions.

It is possible that some surficial photodecomposition occurred under the conditions of the field studies either at the soil surface or during its residence time between the air and the soil. The results of this study are consistent with previous reports of surficial photodecomposition in sandy soils (Gu, 1964).
soil surface and the uppermost sampling device. The photodegradability of trifluralin has been widely reported (Lehman and Cross, 1974; Messer-Smith et al., 1974; Probst et al., 1967; Wright and Watanabe, 1963). However, we were unable to determine the extent of photodecomposition using our field sampling methods and analysis by gas chromatograph. If trifluralin decomposition products are observed in the field, the product source may be difficult to identify since the initial photoproduct might be the same as the initial decomposition product from equipment saturation or soils (Farr and Smith, 1973; Probst and Tepe, 1969 and Probst et al., 1969). Furthermore, the initial and other intermediate products do not accumulate but are rapidly converted to polar products which represent the terminal products of degradation (Lehman and Cross, 1974). Cross and Schmitt (1969) have fully described the difficulties and complexities involved in measuring photodegradation under field conditions. Other workers (Olsen and Watanabe, 1964) have reported that trifluralin does not rapidly photodegrade when in contact with the soil surface.

To further elucidate the soil water and photodecomposition phenomena, we initiated a smaller plot study on 12 June 1972 incorporating both trifluralin and lindane at the same rate. Both have similar vapor pressures, but lindane is not readily susceptible to photodecomposition (Perel, 1953). As concentrations of soil and microclimate data were taken to calculate fluxes of each. Presumably, if the apparent volatilization of these two pesticides differed greatly when daytime micrometeor and microclimate conditions were compared or if the surface soil moisture—volatilization relationships did not agree, then significant trifluralin photodecomposition would be suggested. Under soil and microclimate conditions of this nighttime soil surface and warm daytime soil surface, fluxes and recirculation of both pesticides followed a similar trend over a 24-hour period (Fig. 7A and B). As solar radiation increased, the soil surface directed a water content approaching three molecular layers of absorbed water (Fig. 10), the fluxes of both lindane and trifluralin decreased to very low levels (relative to nighttime fluxes). Lindane had a rather consistently higher flux rate than trifluralin. Similar results were found by Spencer and Clacht (1974) in laboratory studies with non-incorporated trifluralin and lindane. Unlike the 1973 study, the parameters of soil temperature and turbulence had little influence on volatilization when the soil surface was dry.

Later in the season (28 June 1974), data were taken on a clear, sunny day, where surface soil water was maintained by periodic irrigation throughout a 24-hour period. Due to the rain and cloud system present, the conditions were different, but over a 24-hour period. Figure 8A shows little difference between concentrations of the two pesticides at 20 cm. However, during the nighttime, high concentrations of both pesticides were observed. The same type of temperature and turbulence tests as radiation and soil temperature monitoring. The lower levels of trifluralin in comparison with lindane could indicate some photodecomposition of trifluralin, however, it is more likely to derive from other sources, like differences in soil adsorption and rate of vertical diffusion and mass flow to the soil surface which undoubtedly were important controlling processes also. Lindane volatilization rate was greater than trifluralin during the day when the surface soil was dry and water was evaporating, probably because the wind effect has a much greater influence on volatilization of lindane (Spencer and Clacht, 1974) than on trifluralin (Spencer and Clacht, 1973). The major significance of the 13 and 28 June 1974 results was that when adequate water was available at the soil surface, apparent volatilization of both lindane and trifluralin increased, during daylight hours and other factors like turbulent transfer, soil temperature, and evaporative demand were high. During nighttime, when radiation input decreased and the surface zone was rewetted from upward soil water movement and perhaps even from some condensation at the soil surface, the pesticide fluxes increased generally as a function of surface soil water content. However, on days when surface water was adequate, flux of trifluralin was lindane increased during the daytime. This was little reduction in both pesticides volatilization until the surface soil water content was decreased to approximately three molecular layers of adsorbed water. Both pesticides reacted similarly. Adsorption to soil particles upon soil drying was apparently a reversible process, since rapid efflux of pesticide was observed when the surface soil was rewetted by dew or rainfall to above three molecular layers of water. Under conditions where

**Fig. 9—Trifluralin and lindane on evaporating at 20 cm with accompanying temperature and soil on temperatures at Westport and Ca. on 28 June 1974.**

**CONCLUSIONS**

Fluxes of trifluralin and lindane were compared with soil and microclimate data on a diurnal basis. When surface soil water content was low, fluxes increased to very low levels during daytime even though turbulence, soil temperature, and evaporative demand were high. During nighttime, when radiation input decreased and the surface zone was rewetted from upward soil water movement and perhaps even from some condensation at the soil surface, the pesticide fluxes increased generally as a function of surface soil water content. However, on days when surface water was adequate, flux of trifluralin was greater at lindane increased during the daytime. There was little reduction in both pesticides volatilization until the surface soil water content was decreased to approximately three molecular layers of adsorbed water. Both pesticides reacted similarly. Adsorption to soil particles upon soil drying was apparently a reversible process, since rapid efflux of pesticide was observed when the surface soil was rewetted by dew or rainfall to above three molecular layers of water. Under conditions where
the soil surface remained above three molecular layers of water, pesticide fluxes responded to increased soil temperature, turbulence, and atmospheric stability conditions.

ACKNOWLEDGMENT

The authors wish to express their thanks to J. S. Taylor and W. A. Johnson, Chemists, for their assistance in preparing the L. S. L. and the Environmental Protection Agency for their help with pesticide application and preparing the research materials. We are also in debt to R. C. Forrest, R. D. Lowery, and J. F. L. Eder for their efforts in the construction of this equipment and the Environmental Protection Agency for their help with the preparation of the research materials. We are also in debt to R. C. Forrest, R. D. Lowery, and J. F. L. Eder for their efforts in the construction of this equipment and the Environmental Protection Agency for their help in preparing the research materials.

APPENDIX

Terms and Units

- Specific heat of air at constant pressure (calorie/°C)
- Water vapor pressure (mbars)
- Latent heat flux (mm/hour)
- Soil heat flux density (calorie cm² min⁻¹)
- Transfer coefficient at some height: above the soil surface (cm/min)
- Latent heat of sublimation (calorie cm² min⁻¹)
- Pesticide concentration (mg/l)
- Pesticide flux density (mg/cm² min⁻¹)
- Richardson's number
- Net radiation (calorie cm² min⁻¹)
- Diffusion of air (cm/sec)
- Moisture stress (psi cm⁻²)
- Moisture temperature (°C)
- Air velocity (meter/min)
- Viscous resistance (height cm)

LITERATURE CITED