# DATA EVALUATION RECORD

## STUDY 10

CHEM 036101 Trifluralin §163-3

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

STUDY ID 40673601E
Harper, L.A., A.W. White, Jr., R.R. Bruce, A.W. Thomas, and R.A. Leonard. 1976. Soil and microclimate effects on trifluralin volatilization. J. Environ. Qual. 5:236-242.

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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).

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 $ng/m^3$ 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%

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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 $ng/m^3$. 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. EFGWB prefers that $[^{14}C]$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 $R_f$ 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 $4.26 \times 10^6$ $ng/m^3$ 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.

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)

Soil temperature was measured with thermopiles at depths of 0.5, 1, 3, 7, 15, 30, 60, and 120 cm in two field locations (Fig. 1) and the average of the two sample locations was used. Soil samples were taken hourly from six sampling locations at depth intervals of 0 to 0.5 and 0.5 to 1 cm with a spatula, and 1 to 2, 2 to 3, 3 to 4, 4 to 5, 5 to 7, 7 to 9, 9 to 12, and 12 to 15 cm with a 2-cm diameter stainless steel tube sampler. The samples were composited for each depth interval and water content determined gravimetrically.

On 12 June 1974 trifluralin and lindane were applied to a small research plot (20 by 20 m). On 13 and 28 June, the same data were measured as previously but because of limited plot size and fetch problems no crop was planted and profile measurements were made closer (20 to 40 cm) to the soil surface. Conditions selected for data collection were bright sunlight-dry soil and bright sunlight-wet soil (controlled by irrigation). These variable conditions were selected to compare aerial concentrations and volatilization rates of trifluralin with those of lindane, a reference pesticide which is stable in light (Frear, 1955).

## RESULTS AND DISCUSSION

The energy balance method is useful for calculating flux during daylight periods. Large relative errors which occur in the $(\partial e/\partial z)$ and $(\partial T/\partial z)$ terms (Fig. 2) in early morning and late afternoon, and in nighttime periods when net 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 accelerated effort in recent years, no general relationship for diabatic correction has been found (Thom et al., 1975). One correction which seems to work reasonably well under most conditions of thermal stability (Parmele et al., 1972, Thom et al., 1975) is the "KEYPS" profile correction function with parameters developed from an analysis of several data sources (Panofsky et al., 1960). This relationship corrects only for thermal stability and not for the small effect on stability of the humidity gradient (Dyer and Hicks, 1970). Further, superimposed on the potential error due to stability corrections is the uncertainty of inequality of exchange coefficients for pesticide and momentum or energy (Swinbank and Dyer, 1969, Dyer and Hicks, 1970). Equality of exchange coefficients was assumed in all calculations in this report.

Comparisons between the daytime (0800 to 1900, EDT) calculated fluxes for water vapor and pesticide indicated that the momentum balance method typically estimated greater fluxes than the energy balance method. Table 2 gives a comparison of daytime fluxes for 3 days. There was day-to-day variation in pesticide flux calculations, however, on days with higher soil water content, the predictions by the two methods tended to be closer than that on days with drier soil water conditions. (The maximum absolute difference on any day was < 1.5 g ha⁻¹ 11 hours⁻¹.) Differences in calculated water vapor flux ($E$) between the two methods were greater than pesticide flux differences ($P$).

Table 2—Comparison of daytime (0800 to 1900 EDT) water vapor ($E$) and pesticide fluxes ($P$) calculated by the energy balance (eb) and momentum balance (mb) methods, 1973

| Date | $E_{eb}$ | $E_{mb}$ | $P_{eb}$ | $P_{mb}$ |
|---|---|---|---|---|
| | — mm/11 hours — | | — g ha⁻¹ 11 hours⁻¹ — | |
| 27 June | 4.38 | 7.46 | 13.89 | 12.36 |
| 2 July | 4.71 | 9.12 | 0.63 | 1.27 |
| 19 July | 3.38 | 4.11 | 0.52 | 0.59 |

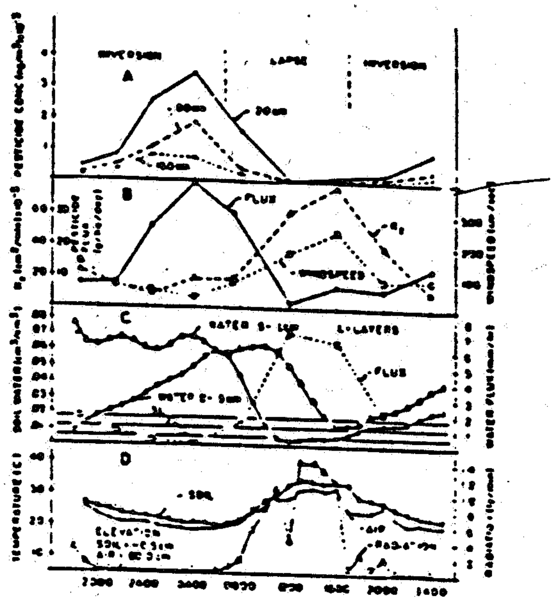

Fig. 3—Calculated trifluralin and water vapor fluxes with related soil and microclimate data, and trifluralin concentrations in air at watershed site P 3, Watkinsville, Ga., on 15–16 June 1973

The momentum balance (mb) method was used to calculate water vapor ($E_{mb}$) and pesticide flux ($P_{mb}$) on a total daily basis to give the amount of water or pesticide passing through a plane 90 cm above the soil surface. Figure 3 shows trifluralin flux along with microclimate data beginning 3.5 hours after application and incorporation. Initial trifluralin flux was quite low even though the highest soil concentration would be expected to occur at this time. The afternoon following trifluralin incorporation was sunny and hot, and soil water evaporation was high. The soil surface zone (0 to −0.5 cm) was depleted of soil water (Fig. 3C) down to an amount equivalent to less than three molecular layers of water adsorbed to the soil particles.[6] Evidently, evaporation of water from the soil surface zone and adsorption of the pesticide decreased the pesticide vapor pressure enough to virtually stop volatilization. Upon cessation of radiation input, the surface soil water content increased, thus increasing the pesticide vapor pressure sufficiently to cause a considerably higher flux rate. When evaporative demand increased again around 0700 hours, surface soil water content and

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[6] The water content equivalent to one, two, and three layers of water was computed by assuming one layer was 3 × 10⁻⁸ cm thick over a measured surface area of 16.8 × 10⁴ cm²/g. An appropriate soil bulk density was then applied to convert water content to a volume basis.

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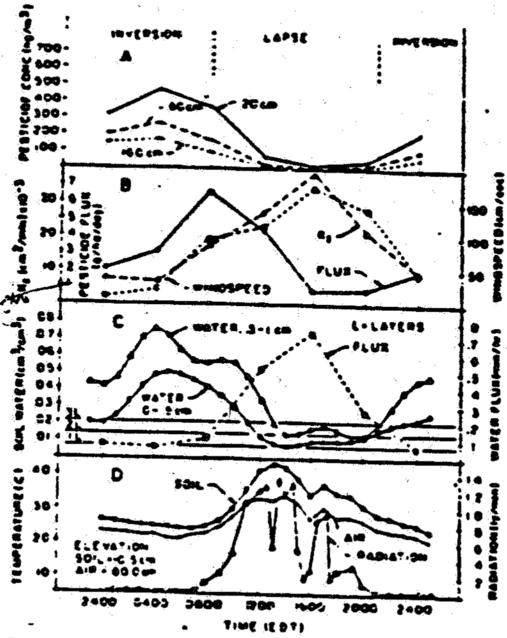

Fig. 4—Calculated trifluralin and water vapor fluxes with related soil and microclimate data, and trifluralin concentrations in air at watershed site P 3, Watkinsville, Ga., on 2 July 1973.

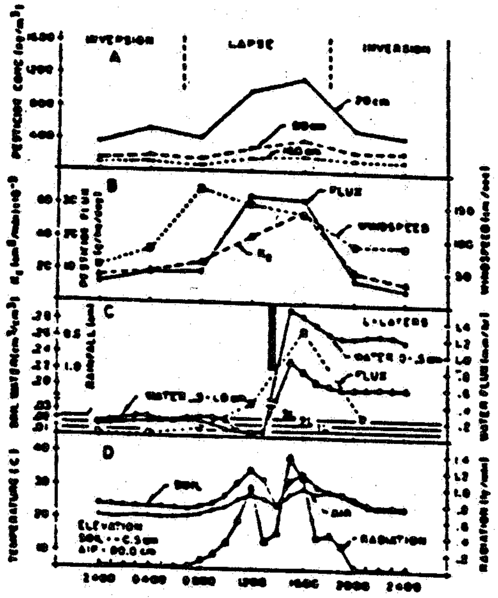

Fig. 5—Calculated trifluralin and water vapor fluxes with related soil and microclimate data, and trifluralin concentrations in air at watershed site P 3, Watkinsville, Ga., on 20 June 1973.

pesticide flux began to decrease. A sharp drop in pesticide flux was observed around 0900 hours when evaporative demand again depleted the surface soil water content down to less than three molecular layers of water. Pesticide flux remained low as long as water content in the surface zone remained below that level. The effects of soil water on pesticide volatilization have been shown under carefully controlled laboratory conditions with several pesticides (Bardsley et al., 1968; Igue et al., 1972; Spencer et al., 1969, Spencer and Cliath, 1976). These controlled studies have demonstrated that pesticide volatilization virtually stops at low soil water contents. Our results indicate that the same principles and relationships between soil water and pesticide volatilization prevail under field conditions.

Previous research (Parmele et al., 1972) has shown an increase in pesticide flux during the daytime which was highly correlated with water vapor flux. Similar to water flux, their pesticide flux decreased near nighttime and was assumed zero during nighttime, however, they did not report relative soil water and temperature data. Under the soil and microclimate conditions of our study, greater fluxes were observed during the day only when adequate surface soil water was available (e.g., 1330 hours, Fig. 5C). On most days, surface soil water was depleted during the daytime and pesticide fluxes were less than those during nighttime when radiation input subsided and the surface soil was rewetted from upward soil water movement and, perhaps, from some surface condensation (See Fig. 3 and 4).

Trifluralin adsorption by the soil is obviously a reversible process since during nighttime when evaporative demand decreases and the surface soil water content increases above three molecular layers of water, the pesticide air concentration and vapor flux increase rapidly (Fig. 3A, B, and C). The effects of soil temperature, windspeed, transfer characteristics, and atmospheric stability seem to have little influence on pesticide flux under this type of soil condition. Similar pesticide flux, soil, and microclimate-related phenomena were observed as the soil was depleted of the pesticide and less was available in the soil for volatilization. During 2 July, the same soil surface control of volatilization was observed (Fig. 4A, B, and C)[7] when the soil surface water content decreased to less than three molecular layers of water.

The process of increased pesticide flux, presumably from pesticide desorption from the soil upon soil rewetting, is vividly shown in the 20 June period (Fig. 5A, B, and C). From midnight until 1200 hours, the soil surface and underlying zone was very dry (even in early morning since there was no dew formation because of impending rain), and pesticide flux and air concentrations were quite low. Then, from 1326 to 1355 hours, 0.93 cm rainfall fell and adequately rewetted the soil surface and underlying zone and caused a rapid efflux of pesticide. This

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[7] Note scale changes. Pesticide flux on 2 and 19 July are one-tenth the scale magnitude of 15-16 and 20 June.

rapid volatilization is reflected in the high average flux during the 1000 to 1400-hour sample even though soil water content was increased only during the last 30 min of the sampling period. After the rainfall, flux responded to other factors in addition to soil water content. It seemed to be affected primarily by turbulence ($K_z$, Fig. 5B) and perhaps to a lesser extent, by soil temperature (Fig. 5D). Atmospheric stability (Fig. 5A) seemed to have little influence on aerial pesticide concentrations, except during the early morning dry period and late evening since the flux dropped slightly while aerial concentrations remained rather constant.

Late in the season (19 July) data were collected after a rain on an overcast, reasonably cool day with adequate water available. There was little change in any soil or microclimate parameters (Fig 6B, C, and D) and little change in pesticide volatilization or air concentrations throughout the day (Fig. 6A and B).

It is obvious that rate-limiting factors which control trifluralin volatilization loss are soil-controlled, since vapor densities observed were only a small fraction of air saturation equilibrium values ($4.29 \times 10^6$ ng/m$^3$ at 30C [Spencer and Cliath, 1974]). The highest observed value at 20 cm after application and incorporation was 3,403 ng/m$^3$ with an air temperature of 25C on 15 June 1973 (White et al., 1976).[4] Spencer and Cliath (1974), passing air through Gila silt loam, reported an equivalent vapor density of approximately $0.2 \times 10^6$ ng/m$^3$ for similar soil concentration and soil water content (1.65 µg/g and 6.0% water, respectively) to our highest flux situation. Our highest air concentration of 3,403 ng/m$^3$ represents approximately 2% of the vapor density corresponding to equilibrium between the atmosphere and soil trifluralin at the soil surface. It is evident that diffusion in air is not rate limiting and rapid dispersal was occurring. Further, residence time within the 20- to 160-cm volume of air (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 3 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 period of the early morning hours (2400 to 0600 EDT). On 19 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. 3A, 4A, 5A, and 6A, there was always a rapid dispersal of volatilized trifluralin even during atmospheric stable conditions.

It is possible that some trifluralin photodecomposition occurred under the conditions of this field study either at the soil surface or during its residence time between the

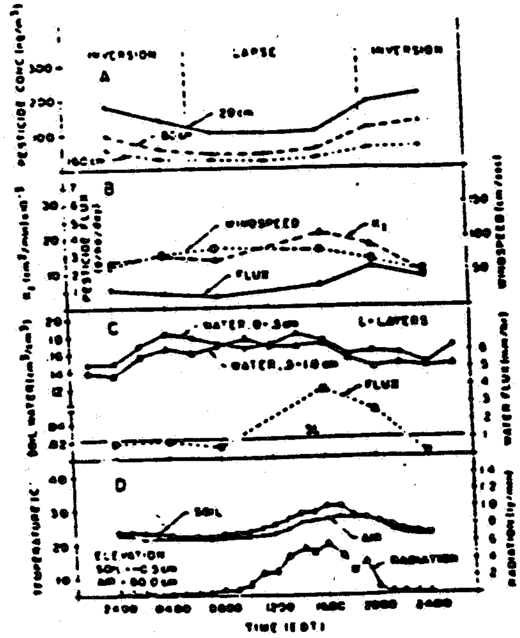

Fig. 6—Calculated trifluralin and water vapor fluxes with related soil and microclimate data and trifluralin concentrations in air at watershed site P 3 Watkinsville, Ga., on 19 July 1973.

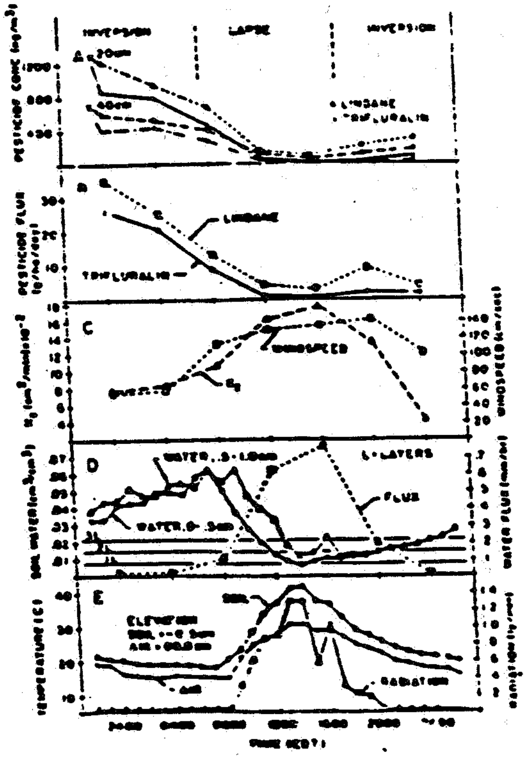

Fig. 7—Calculated trifluralin and lindane fluxes and air concentrations with accompanying soil and microclimate data at Watkinsville, Ga., on 13 June 1974.

soil surface and the uppermost sampling device. The photodegradeability of trifluralin has been widely reported (Leitis and Crosby, 1974, Messersmith et al., 1971; Probst et al., 1967, Wright and Warren, 1965); however, we were unable to determine the extent of photodecomposition using our field sampling methods and analysis by gas chromatography. Additionally, 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 aerobic decomposition in soils (Parr and Smith, 1973, Probst and Tepe, 1969, and Probst et al., 1967). Furthermore, this initial and other intermediate products do not accumulate but are rapidly converted to polar products which represent the terminal products of degradation (Leitis and Crosby, 1974). Crosby and Li (1969) have fully described the difficulties and complexities involved in measuring photodecomposition under field conditions. Others (Wright and Warren, 1965) have reported that trifluralin does not rapidly photodegrade when in contact with the soil surface.

To further elucidate the soil water and photodecomposition phenomenon, we initiated a smaller plot study on 12 June 1974 incorporating both trifluralin and lindane at the same rate. Both have similar vapor pressures, but lindane is not readily susceptible to photodecomposition (Frear, 1955). Air concentrations and soil and microclimate data were taken to calculate fluxes of each. Presumably, if the apparent volatilization of these two pesticides differed greatly when daytime-to-nighttime soil and microclimate conditions were compared or if the surface soil moisture-volatilization relationships did not agree, then significant trifluralin photodecomposition would be suspected. Under soil and microclimate conditions of cool night-moist soil surface and warm day-dry soil surface, fluxes and concentrations of both pesticides followed a similar trend over a 24 hour period (Fig. 7A and B). As radiation intensity increased and the soil surface dried to a water content approaching three molecular layers of adsorbed water (Fig. 7D), 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 Cliath (1973, 1974) in laboratory studies with soil-incorporated trifluralin and lindane. Like the 1973 study, the parameters of soil temperature or 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 equipment failure, data necessary for flux calculations were lost; however, meteorological conditions were very similar to those on 12 June. Figure 8A shows little difference between concentrations of the two pesticides at 20 cm during nighttime. However, during the daytime, aerial concentrations of both pesticides exhibited definite temperature and turbulence (not possible to separate) effects as radiation and soil temperature increased. The lower levels of trifluralin as compared with lindane could indicate some photodecomposition of trifluralin; however, it is more logical to ascribe this to other factors like

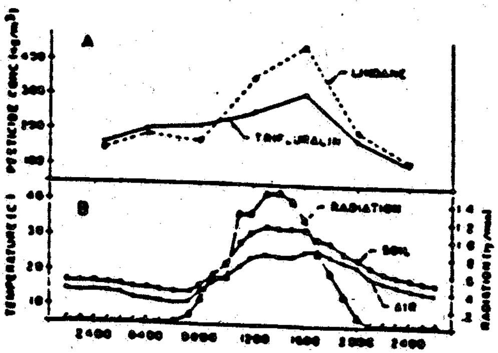

Fig. 9—Trifluralin and lindane air concentrations at 20 cm with accompanying radiation and soil and air temperatures at Watkinsville, Ga., on 28 June 1974.

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 wet and water was evaporating, probably because the wick effect has a much greater influence on volatilization of lindane (Spencer and Cliath, 1973) than on trifluralin (Spencer and Cliath, 1974). 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, or evapotranspiration, dominated volatilization rates. When even a thin layer of surface soil dried to less than approximately three molecular layers of adsorbed water, the surface soil water content dominated volatilization with little further influence by other soil and microclimate effects.

## 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 decreased 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 soil surface water was adequate, flux of trifluralin and lindane increased during the daytime.

There was little reduction in pesticide 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

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## APPENDIX

### Terms and Units

$C_p$ = Specific heat of air at constant pressure (calorie g$^{-1}$°C$^{-1}$)
$e$ = Water vapor pressure (mbars)
$E$ = Latent heat flux (mm/hour)
$G$ = Soil heat flux density (calorie cm$^{-2}$ min$^{-1}$)
$K_z$ = Transfer coefficient at some height $z$ above the soil surface (cm$^2$/min)
$l$ = Latent heat of vaporization (calorie/g)
$p$ = Pesticide concentration (mg m$^{-3}$)
$P$ = Pesticide flux density (g ha$^{-1}$ day$^{-1}$)
$Ri$ = Richardson's number
$R_n$ = Net radiation (calorie cm$^{-2}$ min$^{-1}$)
$\rho$ = Density of air (g/cm$^3$)
$\tau$ = Shearing stress (dynes/cm$^2$)
$T$ = Air temperature (°C)
$u$ = Windspeed (cm/min)
$z$ = Vertical height (cm)
$z_d$ = Effective vegetation height (cm)

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