DATA EVALUATION RECORD

STUDY 7

CHEM 036101 Trifluralin §163-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 40673601B
Spencer, W.F. and M.M. Cliath. 1974. Factors affecting vapor loss of trifluralin from soil. J. Agric. Food Chem. 22:987-991.

DIRECT REVIEW TIME = 10

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11 JUL 1994

CONCLUSIONS:

Mobility - Laboratory Volatility

This laboratory 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 other published volatility data submitted (MRID 40673601A, 40673601C, 40673601D, 40673601E, 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. Data are needed to determine relative rate of dissipation due to volatility in relation to other routes of dissipation.

In this study the concentration of trifluralin in air and soil was not determined or analyzed for or furnished. Therefore, the application rate and material balances could not be confirmed and the concentration of trifluralin residues in the air could not be related to the concentration of trifluralin residues in the soil. In addition, the pattern of decline of the test substance coulld not be established.

METHODOLOGY:

Laboratory volatility

In order to measure vapor density without soil, technical grade trifluralin (purity of 99.5%) dissolved in hexane was added to silica sand with an atomizer (4 g trifluralin:1100 g sand). The hexane was allowed to evaporate and the treated sand was placed in a glass column. Dry nitrogen gas was passed through the trifluralin-treated sand at 3.5 mL/min and through a hexane trapping solution "until sufficient trifluralin had been trapped...for analysis". The hexane solution was analyzed by GLC with electron capture detection.

To measure the effects of trifluralin concentration and moisture content on vapor density, autoclaved silt loam soil (Gila; 18.4% clay and 0.58% organic matter, not further characterized) was treated with trifluralin (technical grade; purity 99.5%) at 2.5-80 ug/g. After the hexane evaporated, the soil moisture was adjusted with water (for water content <6%) or ice (for water contents >6%). The method used to determine the vapor density was not reported.

To determine the effects of organic matter on volatilization, the vapor density of trifluralin was measured in clay soil (Imperial; 68% clay, 0.20% organic matter, not further characterized), Gila silt loam soil, and sandy loam soil (Kentwood; 10.0% clay, 1.62% organic matter, not further characterized). The soil moisture was adjusted to 19% water content and the trifluralin (technical grade; purity 99.5%) concentration was 10.0 ug/g. Columns of soil were prepared and allowed to equilibrate to varying moisture contents for 24 hours prior to vapor density measurements. The method used to determine the vapor density was not reported. The moisture and trifluralin content of soils were measured at the beginning and end of each series of vapor density measurements (method not reported).

To study the volatilization of trifluralin incorporated into the soil, trifluralin (technical grade; purity 99.5%) in hexane was added to autoclaved silt loam soil (Gila) at 10 ug/g. The soil was placed in a column (10 cm length, 4.78 cm id). Nitrogen gas was passed over the surface of soil columns at 809 mL/min; the atmosphere in the headspace was replaced approximately every 3 seconds. The water content of the soil in the columns was 30.5%, the nitrogen gas was adjusted from 100% relative humidity at the start of the study to 0% at the termination. The nitrogen was vented through a hexane or

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ethylene glycol trapping solution. The experiment was conducted for up to 48 days. The method used to determine the vapor density was not reported.

To study the volatilization of trifluralin from the surface of the soil, trifluralin (technical grade; purity 99.5%) in hexane was added to the surface of columns of autoclaved silt loam soil (Gila) at 1, 2 and 10 kg/ha. Columns for surface application volatility testing were wetted from the bottom to 30.5% moisture content. The 2 kg/ha rate was also used to measure volatility at 50 and 100% relative humidity. The method used to determine the vapor density was not reported.

DATA SUMMARY:

Trifluralin (technical grade; purity 99.5%) dissolved in hexane, and incorporated into columns of autoclaved silt loam soil at 10 ug/g, volatilized slowly (half-life not calculated). Total loss for the first 24 hours was 0.0517 kg/ha (0.36% of total applied); total loss for 48 days was 0.342 kg/ha (2.45% of applied). Volatilization was greater at lower relative humidities. When trifluralin was applied to an air dry surface without incorporation, volatilization during the first hour was 0.0014 kg/ha; when application was to a wet surface, losses were 0.142 and 0.153 kg/ha; when the dry soil was wetted from the bottom, volatile loss was 1.97 kg/ha/day. When 1 and 2 kg/ha of trifluralin were applied to moist surface soils, the entire application was volatilized within 24 hours.

In sand, the vapor density of trifluralin (technical grade; purity 99.5%) at 4 g trifluralin:1100 g sand was 0.889 ug/L at 20 C, and was 19.94 ug/L at 40 C. The vapor pressure increased from 0.485×10^{-4} mm to 11.59×10^{-4} mm (Table 1).

COMMENTS:

1. 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 GLC only or or not furnished. The analytical method did not measure the concentration of trifluralin in the carrier gas. Trifluralin was trapped, and the flux was measured as losses per acre.

2. Soil samples were not analyzed for trifluralin; therefore, the pattern of decline of trifluralin from the soil could not be measured, 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.

3. Material balance data were not included.

4. The methods description was inadequate; for example, the incubation conditions and temperature were not reported.

5. The presentation of the data was not clear enough to permit an accurate assessment.

6. Soils used in this study were not completely characterized.

7. The efficiencies of the trapping solutions were not reported.

8. The study author stated that the 10 ug/g application rate used in the incorporation study was equivalent to 14 kg/ha.

9. 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)

Table I. Vapor Density and Apparent Vapor Pressure of Trifluralin at Different Temperatures

Temp, °C	Vapor density, µg/l.	Vapor pressure,* mm × 10^{-4}
20	0.889 ± 0.016	0.485 ± 0.009
30	4.29 ± 0.09	2.42 ± 0.05
40	19.94 ± 0.30	11.53 ± 0.17

* Calculated from vapor density (d) with the equation $P = d(RT/M)$, where P is the vapor pressure, R is the molar gas constant, T is the absolute temperature, and M is the molecular weight.

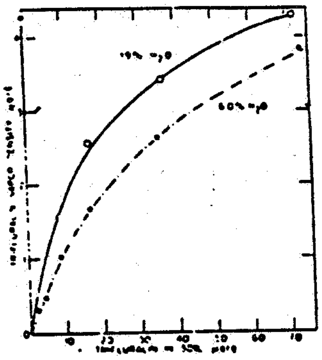

Figure 1. Vapor density of trifluralin as related to concentration in Gila silt loam at 6 and 19% soil water contents and 30°. The asterisk indicates vapor density of trifluralin without soil.

RESULTS AND DISCUSSION

Vapor Density and Desorption Isotherms for Trifluralin. The vapor density and apparent vapor pressure of trifluralin at three temperatures are shown in Table I. The apparent vapor pressure was linearly related to temperature by the equation log P = 17.3[illegible] − 6344/T with ΔH, (heat of vaporization) = 29 kcal/mol. Probst *et al.* (1967) reported that the vapor pressure of trifluralin was 1.99 × 10^{-4} mm at 29.5°. The data in Table I can be used to calculate vapor pressures at other temperatures encountered under field conditions.

The effect of concentration on vapor density of trifluralin in Gila silt loam at 6 and 19% soil water content at 30° is shown in Figure 1. No differences in trifluralin concentrations or soil water contents were measurable between the start and end of a series of vapor density runs. However, the trifluralin concentrations and soil water contents were slightly lower than the planned application rates because of losses during the atomizer spray application. The data reported here are based on the trifluralin concentrations and soil water contents measured rather than the amounts supposedly applied. Vapor density increased rapidly as trifluralin concentration increased, and at 19% water a saturated vapor density equal to that of trifluralin without soil was reached at approximately 73 µg/g. For a saturated vapor at 6% water, the projected trifluralin concentration needed was approximately 95 µg/g. Obviously, the volatility of trifluralin would be greater at 19% than at 6% soil water content. For example, at 10 µg/g the vapor density is 50% greater at 19% than at 6% soil water content.

Figure 2 shows the effect of a wider range of soil water contents on trifluralin vapor density at two trifluralin concentrations. Vapor density was markedly reduced in the drier soil at both trifluralin soil concentrations (8.4 and 72 µg/g), but the vapor density began to decrease at a higher soil water percentage at 8.4 than at 72 µg/g. When the soil water content reached 6%, the vapor density at both trifluralin concentrations was significantly reduced. Air drying the Gila silt loam to approximately 2% water content reduced the vapor density to extremely low values. For example, at soil trifluralin concentrations of 2.1-35 µg/g, the vapor density in air-dry soil ranged only from 0.36 to 0.65 ng/l. At 19% soil water content, the trifluralin vapor density, or potential volatility, was 3000-5000 times greater than when the soil was air dry. As the soil water content was reduced, trifluralin vapor density began to decrease at a higher soil water content than was observed for dieldrin or lindane. Vapor densities of dieldrin at 100 µg/g (Spencer *et al.*, 1969) or lindane at 10 µg/g (Spencer and Cliath, 1970b) in Gila silt loam did not decrease until the soil water content was reduced below approximately

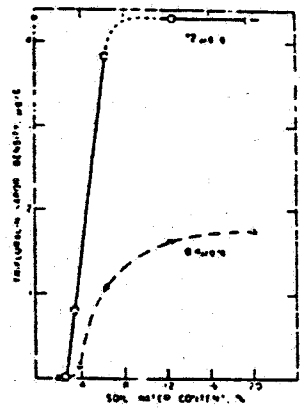

Figure 2. Effect of soil water content on vapor density of trifluralin in Gila silt loam at 8.4 and 72 µg/g of trifluralin and 30°

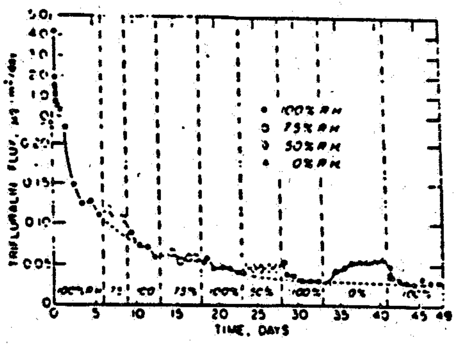

Figure 3. Volatilization rate of soil-incorporated trifluralin as related to time and relative humidity of the N_2 gas passing over the soil surface at 30° with 10 µg/g of trifluralin mixed in Gila silt loam at 50 millibars of water suction (expanded scale first day only).

one molecular layer of water equivalent to approximately 2.7% water in Gila silt loam.

Vapor densities at 10 µg/g of trifluralin in three soils varying in organic matter (O.M.) content were 3.19, 1.73, and 0.62 µg/l. in Imperial clay (0.20% O.M.), Gila silt loam (0.58% O.M.), and Kentwood sandy loam (1.62% O.M.), respectively. Thus, vapor density decreased as O.M. content increased. Since the clay content was inversely related to the O.M. content of the three soils, these results indicate that clay plays a minor role in trifluralin adsorption in wet soil. Evidently, trifluralin adsorption, consequently vapor density or potential volatility, is a function of the O.M. content of the soil, at least in wet soils. Spencer (1970) reported that vapor density of dieldrin was inversely related to the O.M. content of the same three soils.

The decreasing vapor density of trifluralin with increasing soil O.M. content is consistent with data reported by others. Weise *et al.* (1971) reported that the toxicity and persistence of trifluralin in four soils were related to the O.M. content of the soils. Segraves *et al.* (1973) found that in 21 soils the total carbon content of the soil was highly associated with trifluralin activity—91% of the variability in response to rate of trifluralin could be accounted for by total carbon content of the soil, whereas only 55% of the variability was associated with clay content.

Volatilization of Trifluralin from Soil. The volatilization rate of soil-incorporated trifluralin as related to time and water loss rate over a 48-day period is shown in Figure 3. The maximum volatilization rate during the first 15 min was 4.19 µg/cm² per day. This dropped to less than 0.30 µg/cm² per day within 24 hr. The total loss for the first 24 hr was 0.517 µg/cm² (0.0517 kg/ha) or 0.36% of that applied. The total loss by volatilization during the 48 day period was 3.42 µg/cm² (0.342 kg/ha) or only 2.45% of that applied. The rapid decrease in volatilization rate of soil incorporated pesticides with time was also observed with lindane and dieldrin (Spencer and Cliath, 1973). The decreased volatilization of soil-incorporated trifluralin was caused by depletion of trifluralin at the soil surface and not by anaerobic degradation of trifluralin in the soil as reported by Parr and Smith (1973). The Gila silt loam was autoclaved which effectively retarded microbial degradation during the test period.

Volatilization rates were somewhat higher at the lower relative humidities, indicating that evaporating water slightly increased the volatilization rate of trifluralin by the wick effect of transporting trifluralin to the surface in evaporating water. This was most apparent at 50 and 0% relative humidity when water was evaporating at the higher rates, compared to no water loss at 100% relative humidity. The effect of evaporating water on the loss of trifluralin was not nearly as great as was observed with lindane (Spencer and Cliath, 1973). At 100% relative humidity, the trifluralin volatilization rate leveled off at flux values approaching 0.025 µg/cm² per day (0.0025 kg/ha per day). When a period of 100% relative humidity followed a drying period at 0 or 50% relative humidity, the volatilization rate of trifluralin did not increase as did that of dieldrin (Spencer and Cliath, 1973). This indicates that trifluralin volatilized from the surface at approximately the same rate as it moved upward in the evaporating water and, unlike dieldrin, did not accumulate at the surface during drying.

Trifluralin volatilized much more rapidly when applied on the soil surface than when mixed into the soil. Figure 4 shows volatilization of trifluralin applied on the wet surface of Gila silt loam at the rate of 1, 2, and 10 kg/ha with the N_2 passing over the soil surface at 100% relative humidity. Initially, volatilization was almost the same for all three application rates, but volatilization for the 1- and 2-kg/ha applications decreased much more rapidly than for 10 kg/ha with time due to more rapid surface depletion. The maximum volatilization rate from each surface treatment was approximately 40 µg/cm² per day (4 kg/ha per day) compared with a volatilization rate of 0.0517 kg/ha per day for the first 24 hr after soil incorporation. With surface applications, the volatilization rate during the initial period of measurement (either 15 or 30 min) was lower than that measured during the second or third volatilization period. This was probably caused by a reduced trifluralin vapor pressure in the presence of hexane before its complete evaporation during the first few minutes of measurement.

Figure 5 shows volatilization rates of surface applied trifluralin at 2 kg/ha when applied (a) to a wet soil with the N_2 gas at 100% relative humidity, (b) to a wet soil with the N_2 at 50% relative humidity, and (c) to an air-dry soil which was wetted after 8 to 9 hr of volatilization. With the wet soil surface, passing 50 and 100% relative humidity air over the soil resulted in no significant differ-

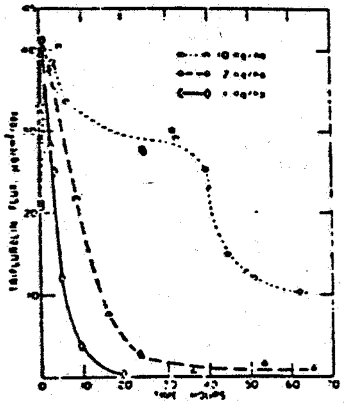

Figure 4. Volatilization of trifluralin at 30° and 100% relative humidity applied on a wet soil surface of Gila silt loam at 10, 2, and 1 kg/ha

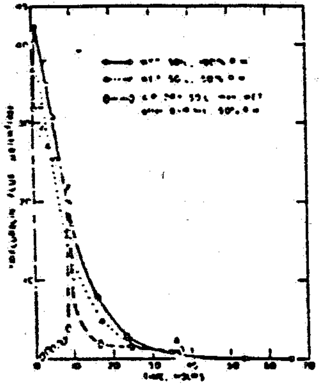

Figure 5. Volatilization rates of surface-applied trifluralin at 2 kg/ha as related to relative humidity of the N_2 gas and the water content of the soil surface.

ences in volatilization rate. When trifluralin was applied to an air-dry soil surface, very low volatilization rates resulted. Vapor loss during the first hour was 0.0014 kg/ha from the dry surface application as compared with vapor losses of 0.142 and 0.153 kg/ha for the wet surface applications. The volatilization rate increased between 1 and 8 hr before the soil was wetted, because of water vapor adsorption by the soil from the 50% relative humidity carrier gas. When the dry soil was wetted, volatilization increased to 19.7 ng/cm² per day (1.97 kg/ha per day). In a duplicate column when 2 kg/ha of trifluralin was surface applied to the air dry soil, without subsequent wetting, essentially all of the trifluralin was extracted from the soil column after 2.25 days of volatilization.

When trifluralin is surface applied to a moist soil, trifluralin concentrations are above that needed for a saturated vapor, and volatilization is at a rate similar to unadsorbed trifluralin. For example, 1 and 2 kg/ha of trifluralin applied to wet soils were essentially vaporized in less than 24 hr. The rapid vapor loss from surface applications to moist soils indicates that trifluralin must be incorporated immediately to prevent excessive loss. However, when applied to a dry soil surface, volatilization is extremely low and incorporation probably can be delayed until a more convenient time. Trifluralin concentration and soil water content effects on vapor density and volatilization are consistent with data on trifluralin activity and dissipation rates reported by other investigators (Standifer and Thomas, 1965; Bardsley *et al.*, 1967, 1968; Hollist and Foy, 1971).

The high volatilization rates from surface applications indicate that vapor loss is the major reason for the lack of herbicidal activity from surface applications, but does not rule out the possibility of photochemical decomposition being a significant pathway for loss of surface-applied trifluralin under some conditions. Ultraviolet light from sunlight probably decomposes trifluralin on the soil surface, as well as in the vapor phase following volatilization.

The exact relation between volatilization rates measured in laboratory columns and those expected in the field is unknown. In the field, volatilization rates from surface applications probably would be higher than those reported herein because of higher rates of air exchange under most field conditions. The gas over the soil columns was exchanged, on the average, once every 3 sec which is equivalent to a linear flow rate of only 0.039 mile/hr. This is relatively low compared to windspeeds encountered in most agricultural areas. Consequently, for a wet soil, the maximum volatilization rate of surface-applied trifluralin (approximately 4 kg/ha per day) is probably below the maximum rates that would occur under many field conditions. However, volatilization rates of soil-incorporated trifluralin in the field probably would be similar to those reported here since the rate of loss would be controlled more by the rate of trifluralin movement to the soil surface than by the rate of air exchange over the soil surface.

High volatilization rates, such as those observed from surface applications of trifluralin, undoubtedly occur with most pesticides, but at differing rates depending on their vapor pressures (Spencer *et al.*, 1973). Many pesticides applied to foliage and nonabsorbing surfaces have vapor pressures similar to trifluralin; therefore, similar volatilization rates could be expected. Such high rates of volatilization contribute to the short-term effectiveness of many insecticides, the low use-efficiency of some herbicides, and the environmental contamination with pesticides.

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