

US EPA ARCHIVE DOCUMENT

DATA EVALUATION RECORD

STUDY 11

CHEM 036101

Trifluralin

§163-3

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

STUDY ID 40673601F

White, A.W., Jr., L.A. Harper, R.A. Leonard, and J.W. Turnbull. 1977.
Trifluralin volatilization losses from a soybean field. J. Environ. Qual.
5:105-109.

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11 JUL 1994

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, 40673601E, 40673601G) do indicate the following:

1. Volatility may be a major route of dissipation for trifluralin.
2. Trifluralin appears to volatilize (\approx 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 ("Cecil 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 July 1973. The trifluralin was incorporated to 7.5 cm and the plot was planted to soybeans. During application and incorporation of trifluralin, air samples were collected at temporary sampling sites; permanent sampling masts were set up after planting. 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 were collected at 0, 1, 2, 6, 18, 35, 49, 63, 76, and 120 days. The soil was sampled at each sampling interval at 0- to 0.5-cm and 0- to 7.5-cm depths. Soil was collected from 12-15 sites within two designated areas with a trough-shaped spatula for the shallow samples, and a 2-cm diameter corer for the deeper samples. The soil samples from the same sampling interval and soil depth were composited.

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%.

The soil (50 g) was extracted three times with hexane:acetone (41:59, v:v). The hexane extracts were combined, washed with water, and chromatographed on a florisil column prior to GC analysis as described above. Recovery efficiency of trifluralin from soil was 95%.

DATA SUMMARY:

Trifluralin (44.5% EC) volatilized from sandy loam soil that was treated at 1.17 g/ha in July 1973; the maximum air concentrations of trifluralin were 16,500 ng/m³ immediately posttreatment; at 2, 6, and

18 days posttreatment, air concentrations were 3400 ng/m³, 1150 ng/m³, and 470 ng/m³, respectively. After 35 days posttreatment, the maximum air concentration never exceeded 100 ng/m³ (text and Figure 1). The flux during the application period was calculated to be 722 g/ha/day; for the rest of the application day it was 10 g/ha/day. In the soil after 120 days, 89% of applied trifluralin was gone from the 0- to 7.5-cm depth; volatile losses accounted for 25.9% of the total applied herbicide.

COMMENTS:

1. The trifluralin concentrations in the soil immediately posttreatment were not reported. Soil trifluralin concentrations were reported for 1 day posttreatment; the percent volatiles from this sampling interval indicated that significant volatilization had already occurred. 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.
2. In addition, this study does not meet Subdivision N guidelines because weather data for the study period was incomplete. Tabular climatic data was included for the day of, and prior to, each sampling date. The study author stated that "no unusual extremes in weather conditions occurred during any of the air-sampling periods" during the study.
3. Cumulative losses for the study period (excluding day 0) were 25.1 g/ha.
4. The soil CEC and soil adsorption K value for trifluralin were not included.
5. The study authors reported that there was a general trend for higher volatilization at night than during the day.
6. All data reported for this review came from the text because the data tables were illegible.
7. EFGWB 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 R_f of reference standards.

In this study aliquots of the extracts were analyzed by GC.

8. 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)

RESULTS AND DISCUSSION

Climate data for each day of sampling and the previous day are shown in Table 1. The data presented are typical seasonal measurements for this location in Georgia. No unusual extremes in weather conditions occurred during

any of the air-sampling periods during the 120-day study. There was rainfall immediately before or during three of the sampling periods.

Changes in atmospheric trifluralin concentrations at three heights above the soil are shown for 9 sampling days in Fig. 1. Points shown are average values for air samples taken at the same height from two masses and are the mid-points of 3-, 4-, or 12-hour intervals, except for the 77-min sampling period during application and incorporation on day 1. There were distinct concentration gradients throughout the study with the concentrations highest at the lowest sampling levels.

Trifluralin air concentrations were highest during the application and incorporation period when a level of 16,500 ng/m³ was recorded at the 20-cm sampling height. Air concentrations measured during the application period are shown as isolated points in Fig. 1, since conditions during this period were distinctly different from all other time intervals sampled. Samples were collected from the time spraying started until all the trifluralin had been incorporated. Thus, these measurements reflected the combined effects of spray drift, vaporization from spray droplets, and volatilization from the soil surface before and during trifluralin soil incorporation.

Generally, air concentrations decreased rapidly during the first month. After incorporation, trifluralin concentrations in air at 20 cm reached a maximum of 3,400 ng/m³ at 0400 on day 2 (Fig. 1), 1,150 and 470 ng/m³, respectively, on days 6 and 18, and after day 35 maximum concentrations never exceeded 100 ng/m³.

The seasonal trends in average daily trifluralin air concentrations at the 80-cm height and in trifluralin soil concentrations at two depths (0 to 0.5 and 0 to 7.5 cm) are shown in Fig. 2A and 2B. These data clearly show that soil and air concentrations decreased with time during the season. However, average daily trifluralin air concentrations (Fig. 2A) did not satisfactorily indicate the possible range differences in levels at any given time interval (Fig. 1).

Figure 2B shows that during the first 35 days the 0- to 0.5-cm surface soil samples had a higher trifluralin content than samples at the 0- to 7.5-cm depth. After 35 days, the trifluralin levels at the two sampling depths were similar. The higher initial levels in the surface samples were due to nonuniform incorporation. Previous studies with the incorporator used in this study showed that 90% of a soil-incorporated herbicide remained in the upper 2.5 cm, with concentrations rapidly decreasing to the 7.5-cm level. Our observed soil trifluralin dissipation rate was

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Table 1.—Climate data and weather conditions for selected days during the study.

| Date | Sample hr | Rainfall mm | Cumulative mm | Wind km | Air Temp Range | | General conditions |
|---------|--------------|----------------|------------------|------------|----------------|-----------|------------------------|
| | | | | | Max °C | Min °C | |
| 15 June | 1 | — | 0.13 | 24 | 20.0 | 19.4 | Fair |
| 16 June | 3 | — | 0.76 | 43 | 20.6 | 19.4 | Fair |
| 19 June | — | — | 0.86 | 23 | 21.1 | 19.4 | Fair |
| 20 July | 6 | 0.00 | 0.43 | 10 | 24.9 | 21.1 | Cloudy, overcast |
| 1 July | — | — | 0.71 | 35 | 22.2 | 20.0 | Fair |
| 2 July | 16 | — | 0.64 | 19 | 22.0 | 20.6 | Fair |
| 19 July | — | — | 0.60 | 43 | 20.6 | 19.4 | Fair |
| 19 July | 20 | 0.00 | 0.33 | 3 | 20.9 | 21.1 | Cloudy, overcast |
| 1 Aug | — | 0.60 | 0.41 | 20 | 20.6 | 21.7 | Cloudy, overcast |
| 2 Aug | 00 | — | 0.26 | 9 | 20.3 | 21.7 | Cloudy, overcast |
| 15 Aug | — | — | 0.00 | 21 | 20.0 | 20.0 | Fair, partly cloudy |
| 16 Aug | 63 | — | 0.36 | 15 | 20.0 | 18.3 | Fair, partly cloudy |
| 28 Aug | — | — | 0.11 | 20 | 22.0 | 17.2 | Fair |
| 29 Aug | 76 | — | 0.00 | 24 | 22.0 | 17.2 | Fair |
| 11 Oct | — | — | 0.36 | — | 22.3 | 22.2 | Fair |
| 12 Oct | 120 | — | 0.01 | — | 21.7 | 11.1 | Fair |

1 Rainfall from 1720-1830 EDT. Storm started cloudy and clearing after 1400.
 2 Rainfall from 0000-1045 EDT. Storm clearing after 1430.
 3 Rainfall from 1745-1830 EDT.

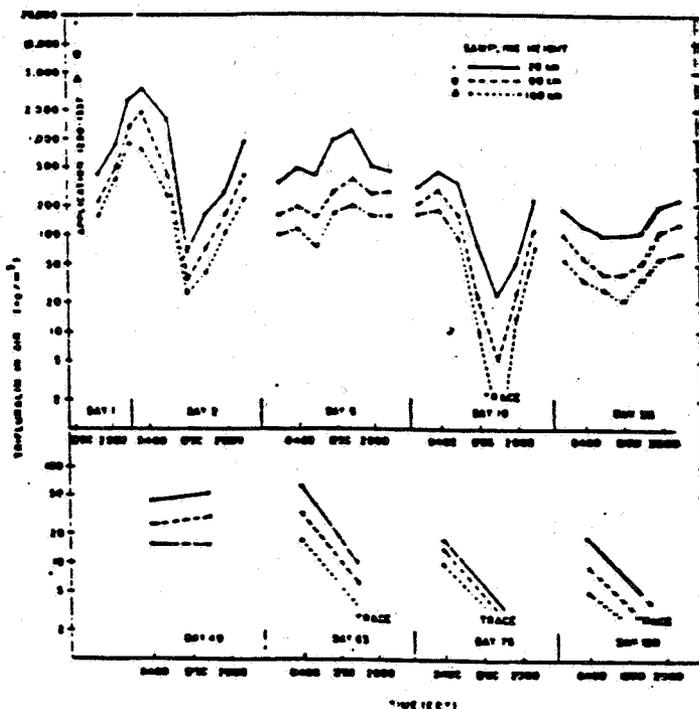


Fig. 1.—Trifluralin atmospheric concentrations at 20 cm and 150 cm above the soil on 9 sampling days during the season.

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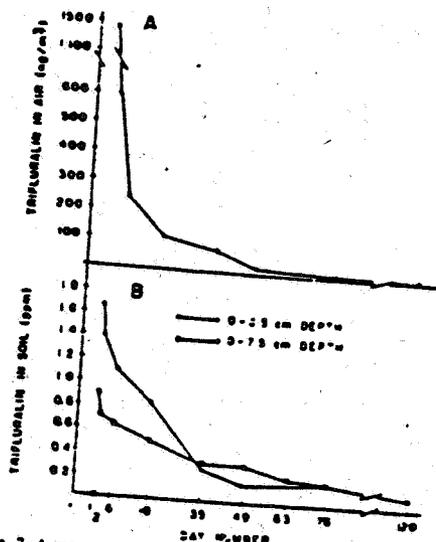


Fig. 2—Average daily trifluralin concentrations in air at the 60 cm height and in soil at the 0 to 25 and 25 to 75 cm depths over 120 days.

comparable with those reported previously by other researchers. Savage (1973) reported that soil trifluralin concentrations decreased rapidly after application and reached low residual levels of < 0.1 ppm in 3 to 4 months. Smith and Wiese (1973) reported soil levels of about 0.1 ppm 1 month after trifluralin soil incorporation in the field. Probst et al. (1967) showed that after 29 and 43 days, 35 and 20%, respectively, of the original trifluralin remained in the soil.

Under certain atmospheric conditions air concentrations of trifluralin varied considerably (Fig. 1). For example, at the 20-cm level on day 2, the trifluralin air concentrations decreased from the maximum of $3,400$ ng/m³ at 0400 to 50 ng/m³ at 1200, and on day 18 air concentrations ranged from a nighttime high of 470 to 23 ng/m³ during the day. We observed very large decreases from nighttime to daytime levels like these on 5 sampling days. In contrast, on days 6, 35, and 49 the sharp decreases between night and day trifluralin concentrations did not occur, and on day 6 the highest trifluralin levels were measured during the day. These latter 3 sampling days differed from the others primarily because rainfall occurred either just before or during the sampling period (Table 1) and soil moisture was generally higher (Harper et al., 1976). Willis et al. (1977) reported that changes in atmospheric concentrations of some pesticides seemed to be related to climatological differences. In another field study, Willis et al. (1972) showed that soil moisture affected diel trifluralin volatilization losses. Spencer and Clath (1974) showed in the laboratory that the potential volatility of trifluralin was 3,000 to 5,000 times greater in moist than in dry soil. Air concentrations of pesticides under field condi-

tions can be influenced by many factors, including soil moisture, wind, temperature, and relative humidity. In this same study Harper et al. (1976) examined in detail the relationships between these variables and trifluralin volatilization and concluded that surface soil moisture was the major factor influencing trifluralin air concentrations and fluxes. On days when the surface soil was dry, trifluralin concentrations dropped sharply. The influence of increased moisture on trifluralin volatilization is clearly seen on day 6 (Fig. 1). A 0.93-cm rain fell at 1326, wetting the soil surface and evidently promoting volatilization, resulting in maximum aerial concentrations during the mid-day and afternoon sample periods for that day.

Trifluralin present at the soil surface and in the vapor phase after volatilization would be subject to degradation by ultraviolet light and likely there was some trifluralin photodecomposition under our study conditions. Losses by this pathway could have contributed to the decreased trifluralin air concentrations that we observed during the daytime for some of the sampling periods, but we were not able to confirm this.

Figure 3 shows volatilization rate losses expressed as trifluralin flux (in g ha⁻¹ day⁻¹), and cumulative losses during the 120-day season. We calculated losses for each sampling time interval, utilizing the atmospheric concentration data of Fig. 1, with accompanying microclimatological measurements, as described by Harper et al. (1976). Trifluralin flux generally decreased with time during the season, when it was expressed on an average daily basis. Flux during the application period (estimated that computed for day 1). During the 7-min application period, the rate was 722 g ha⁻¹ day⁻¹, whereas the average flux for the remainder of that day was 10 g ha⁻¹ day⁻¹. The estimated loss for the application period was 38.6 g/ha and for the remainder of day 1 (about 19.5 hours), 4.4 g/ha. Cumulative losses for the season, estimated as the integral of the flux rate curve, were 251 g/ha, excluding the application period loss. The flux rate for day 6 was slightly higher than that computed for day 2, probably because of the influence of rainfall that day which caused higher daytime atmospheric concentrations of trifluralin and increased volatilization rates. Actual seasonal losses may also differ slightly from that estimated, due to other rainfall events.

Table 2 summarizes seasonal trifluralin losses into the atmosphere and estimated losses by other pathways. We estimated the seasonal volatilization loss, excluding that for the application period, as 22.4% of the applied herbicide. Vapor losses during the application period were greater than during any other period of the study and amounted to 3.5% of the herbicide applied. Thus, total calculated atmospheric losses for the season were 25.9% of the total applied herbicide, with 13 and 19% of the atmospheric loss during application and through day 1, respectively. About half was lost during the first 9 days, and 90% during the first 35 days.

Although our data indicate that trifluralin volatilization losses were relatively high during application, as compared with other periods, an application loss of only 3.5% indicates that the application was quite efficient. Other researchers, using similar ground-sprayer or sprayer-trifluralin, have consistently reported $> 95%$ application ef-

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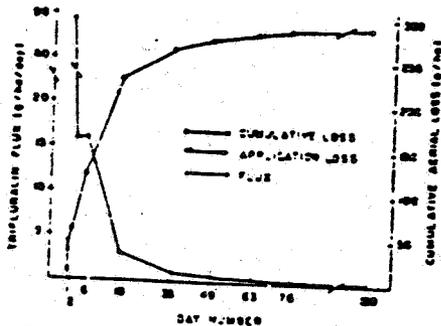


Fig. 3—Visualizer of rate and cumulative losses of trifluralin over a 100-day period in the field.

Sciences (K. E. Savage, personal communication). After 100 days 80% of the originally applied trifluralin had disappeared from the 0-7.5 cm soil zone (Table 2). The combined trifluralin losses by pathways other than volatilization amounted to 63%, almost 2.5 times more than the calculated atmospheric losses. Other work on this same experimental material demonstrated that trifluralin losses in runoff were < 1% (unpublished data, USDA ARS Watkins, Ga. and Southeast Environ. Res. Lab., EPA, Athens, Ga.). Literature reports indicated that trifluralin is not readily leached in soils (Probst et al., 1967; Anderson et al., 1968; Smith, 1972). This suggests that major trifluralin losses in this study probably occurred via other routes, perhaps by non-volitional or physicochemical degradation, as suggested by Kneiss and Topp (1971) and Muehlstein et al. (1971), and by microbial action (Pam and Smith, 1973).

Our estimate of cumulative seasonal trifluralin losses (25.5%) represents volatilization from soil incorporated trifluralin under the soil and climate conditions of this study. Pesticide loss rates will differ for other conditions and factors. Soil clay and organic matter contents influence pesticide adsorption in soil and, thus, control pesticide vapor pressures and potential volatilization (Spencer and Cluth, 1972). At our study site, the soil clay and organic matter content were low. Methods of incorporation affects herbicide persistence and effective-

Table 2—Trifluralin volatilization losses, amounts remaining in soil, and estimated losses via other pathways for the 100 day field test.

| Time (day) | Cumulative volatilization | | Remaining in soil % of applied | Estimated other losses % of applied |
|-------------|---------------------------|-------------------|--------------------------------|-------------------------------------|
| | % of applied | mg/m ² | | |
| Application | 100 | 100 | 100 | 0 |
| 1 | 33 | 33 | 67 | 0 |
| 2 | 52 | 52 | 48 | 0 |
| 5 | 69 | 69 | 31 | 0 |
| 10 | 80 | 80 | 20 | 0 |
| 20 | 88 | 88 | 12 | 0 |
| 40 | 93 | 93 | 7 | 0 |
| 62 | 95 | 95 | 5 | 0 |
| 76 | 96 | 96 | 4 | 0 |
| 100 | 97 | 97 | 3 | 0 |

* Based on amount of trifluralin in soil at 0 to 7.5 cm depth in randomized rows of corn 12.5 m apart at application time was 1.22 kg/ha.

ness depending on the technique and incorporation depth (Robison and Fencler, 1968; Smith and West, 1973). Savage and Barron (1969) showed that trifluralin persistence and volatilization were directly related to depth of soil incorporation. Since our incorporation method left most of the herbicide on the surface 2.5 cm, the measured aerial losses might be expected to be higher than those where more effective incorporation methods were employed. Additionally, volatilization losses were determined indirectly by mathematical methods, which have potential errors (Hart et al., 1976; Parnelle et al., 1972). Thus, many factors must be considered when extrapolating the reported volatilization losses to different situations.

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