

# Volatility of Ethalfluralin, Trifluralin, and Triallate from a Field following Surface Treatments with Granular Formulations

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Losses of ethalfluralin, trifluralin, and triallate vapors to the atmosphere, following unincorporated surface applications of their granular formulations, were compared over a 14-day period. Then, following two incorporations three days apart into the top 5 cm of the field surface, volatility losses were monitored for a further 10 days. Vapor losses were determined using the aerodynamic method for flux measurement with air samples being collected at 30-, 50-, 75-, 100-, 150-, and 200-cm heights above the soil surface. A total of 21% of the applied triallate, 18% of the applied trifluralin, and 14% of the initial ethalfluralin were lost by volatilization over the 24-day period. Volatility losses were associated with rainfall events, and when the soil surface was dry such losses were negligible.

**Keywords:** *Field study; granular formulations; ethalfluralin; triallate; trifluralin; volatility*

## INTRODUCTION

Ethalfluralin [*N*-ethyl-*N*-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl)benzenamine], trifluralin [2,6-dinitro-*N,N*-dipropyl-4-(trifluoromethyl)benzenamine], and triallate [*S*-(2,3,3-trichloroallyl)diisopropylthiocarbamate] are used in western Canada as pre-emergence soil-incorporated herbicides for the control of a variety of weeds in cereal, oilseed, and legume crops.

Ethalfluralin, triallate, and trifluralin are all considered to exhibit moderate volatility at 25 °C, with vapor pressures of  $0.82 \times 10^{-4}$ ,  $1.93 \times 10^{-4}$ , and  $1.11 \times 10^{-4}$  mmHg, respectively (Grover et al., 1988; WSSA, 1989). Because of the volatile nature of emulsifiable concentrate (EC) formulations, soil incorporation is considered necessary to reduce evaporative losses to the atmosphere following application. The three herbicides have low water solubilities and are strongly adsorbed to soil organic matter. Some of their major physical properties are summarized in Table 1.

The dissipation of triallate and trifluralin from mixed EC formulations into the air, following field application and soil incorporation to 5 cm, has been reported (Grover et al., 1988) under western Canadian conditions. Total losses of triallate and trifluralin for the 67-day study period were 18% and 24%, respectively, of those applied, with about half of the losses occurring during the first week after application.

In western Canada, weed control practices using granular formulations of ethalfluralin, trifluralin, and triallate are being considered where the granules would be applied to the field surface in spring with delayed incorporation. Between application and incorporation, volatilization of the active ingredients into the air may be expected. Since no data exist to assess such volatility under Canadian prairie conditions, the present study was undertaken to compare the amounts of ethalfluralin, trifluralin, and triallate vapors released into the atmosphere over a 14-day period following unincorporated surface applications of the granular formulations. Then, following two soil incorporations into the top 5 cm, with a three-day interval between the first and the second, volatility losses were monitored for several further days.

Vapor losses were determined using the aerodynamic gradient method for flux measurement, which has been

used at the Regina Research Station to assess field volatility losses of the herbicides 2,4-D iso-octyl ester (Grover et al., 1985), diclofop-methyl (Smith et al., 1986), triallate (Grover et al., 1988), trifluralin (Grover et al., 1988), and bromoxynil *n*-butyrate and iso-octanoate (Grover et al., 1994).

## MATERIALS AND METHODS

**Location.** The site was a field at the Agriculture and Agri-Food Canada Regina Research Station (Regina, SK). Soil type at the study area was a Dark Brown Chernozemic clay. Soil analyses, conducted by the Plains Innovative Laboratory Services (Saskatoon, SK), gave mean clay, silt, and sand contents of 69%, 19%, and 12%, respectively, an organic matter content of 3.2%, and a pH value of 8.4. Field capacity (moisture at  $\frac{1}{3}$  bar) was 40%.

In the spring of 1995 the site had been cropped with wheat. After fall harvest the field was cultivated and left to overwinter. By May of 1996, the soil surface was finely divided with some trash cover. No further tillage or site preparation was carried out. The site had previously received applications of triallate and trifluralin but not ethalfluralin. Analysis of the 0–10-cm soil layer of four areas (see below) on 6 May 1996 indicated a mean of <10 (background amounts), 48, and 65 gm ha<sup>-1</sup>, respectively, of ethalfluralin, trifluralin, and triallate (Table 2). Given the actual (see later) application rates of triallate (1.28 kg ha<sup>-1</sup>) and trifluralin (0.99 kg ha<sup>-1</sup>), it was considered that the concentrations of these herbicides already present in the soil would be 5% of that being applied, and would therefore not affect the study results. A circular area 300 m in diameter (7.07 ha) was selected as the treatment area. Air sampling equipment and micrometeorological equipment were installed in the center of the field. On the morning of 31 May 1996, three days after the application of ethalfluralin, trifluralin, and triallate, the study area was sprayed with recommended rates of a commercial EC formulation of glyphosate and dicamba to control germinating volunteer wheat and annual weeds.

**Chemicals.** Avadex 10G, a commercial granular formulation containing 10% triallate incorporated into an attapulgite and montmorillonite clay mixture, was purchased from Saskatchewan Wheat Pool (Regina, SK). Edge Granular and Heritage 5G, commercial granular formulations containing 5% ethalfluralin and trifluralin, respectively, were obtained from DowElanco Canada Inc. (Saskatoon, SK) and from Saskatchewan Wheat Pool. In both cases, the active ingredients were adsorbed onto very finely divided limestone particles.

The diameters of the three granular formulations were measured using a Quantimet 970 Image Analyser (Cambridge

**Table 1. Physical Properties (25 °C) of the Herbicides Studied (from Grover et al., 1979, 1988, and WSSA, 1989)**

	vapor pressure (mmHg)	vapor density ( $\mu\text{g L}^{-1}$ )	water solubility ( $\mu\text{g L}^{-1}$ )	Regina clay $K_{OC}$ (adsorption coeff)	$K_{WA}$ (partition coeff)
ethalfuralin	$0.82 \times 10^{-4}$	1.47	300	<i>a</i>	204
triallate	$1.93 \times 10^{-4}$	3.17	4000	1409	1262
trifluralin	$1.11 \times 10^{-4}$	2.00	300	5542	150

<sup>a</sup> Data not available.

**Table 2. Residues of Ethalfuralin, Trifluralin, and Triallate Recovered from Top 10 cm of Field Soil on 6 May and on 17 June 1996**

date	residues remaining <sup>a</sup>					
	ethalfuralin		trifluralin		triallate	
	kg ha <sup>-1</sup>	% appl	kg ha <sup>-1</sup>	% appl	kg ha <sup>-1</sup>	% appl
6 May	<10		48 ± 17		65 ± 22	
17 June	250 ± 36	24 ± 3	373 ± 64	38 ± 6	515 ± 42	40 ± 3

<sup>a</sup> Mean and standard deviation from four replicates. The granular formulations were applied on 28 May 1996.

Instruments, Cambridge, England). Mean diameters with standard deviations for Avadex, Edge and Heritage granules were  $0.56 \pm 0.16$ ,  $0.34 \pm 0.08$ , and  $0.57 \pm 0.13$  mm, respectively.

**Application.** Between 0830h and 1130h on 28 May 1996 (day 1), the study area was consecutively treated with unincorporated surface applications of Avadex 10G, Edge Granular, and Heritage 5G. The granules were applied using a Beline 816 ground-driven granular applicator calibrated to deliver 1.4 kg of a.i. triallate ha<sup>-1</sup> and 1.1 kg ha<sup>-1</sup> of a.i. ethalfuralin and trifluralin. The 9.14-m boom was equipped with 15 outlets at 60-cm spacings. Boom height was 60 cm above the soil surface. During the application period wind speed at 2.0 m varied between 11.2 and 24.5 km h<sup>-1</sup> with a mean of 15.1 km h<sup>-1</sup>. By determining the weight of the granules in the applicator hopper before and after treatment, the actual application rates were determined to be 1.06, 0.99, and 1.28 kg of a.i. ha<sup>-1</sup> for ethalfuralin, trifluralin, and triallate, respectively.

**Incorporation.** Between 0830h and 1000h on day 15 of the study (11 June 1996, 14 days after initial application), the surface herbicides were incorporated into the top 5 cm of the soil surface using a cultivator. Three days later (day 18 of study), a similar incorporation (between 0830h and 1000h) at right angles to the first was carried out. These incorporations follow current application guidelines for ethalfuralin, trifluralin, and triallate (*Crop Protection Guide*, 1996).

**Air Sampling.** Sampling commenced at 1200h on 28 May 1996 (day 1), with the air being sampled at 2-h intervals, day and night. Air samples were collected at 30-, 50-, 75-, 100-, 150-, and 200-cm heights above the treated soil surface using thermally conditioned particulate adsorption-based air traps (Cessna and Kerr, 1993). Each of the vapor traps consisted of minitubes (38 mm × 2 mm i.d.) packed with approximately 14 mg of Tenax-TA resin (Canadian Centre for Advanced Instrumentation, Saskatoon, SK). The tubes were protected from sunlight to prevent possible photochemical degradation of trapped dinitroaniline compounds during sampling. The absence of such degradation was confirmed (data not presented) by separate experiments. Air flow rate was set at 300 mL min<sup>-1</sup> from day 1 to day 12, with sampling being carried out at 2-h intervals. Each flow rate was measured at the beginning and end of the sampling period, and the average air volume sampled was calculated. Prior studies confirmed that there was no significant breakthrough by desorption (<1%) of ethalfuralin, trifluralin, and triallate from minitubes fortified with 100 ng of each herbicide, followed by 2-, 4-, and 5-h aspiration periods at an air flow rate of 300 mL min<sup>-1</sup> (total air volumes of 36, 72, and 90 L, respectively). Between day 13 and prior to the first incorporation on day 15, sampling times, especially at night, varied from 4 to 12 h. For these sampling times, the air flow rates were reduced to 150 or 50 mL min<sup>-1</sup>, with the total volume of air sampled always being less than 90 L.

During the two soil incorporations no air samples were collected. After completion of the first soil cultivation at 1000h on day 15, air sampling was maintained at 2-h intervals for 48 h. Following completion of the second cultivation at 1000h on day 18, sampling was carried out at 2-h intervals for 24 h. At other times, and until the end of the study (day 24, 20 June 1996), sampling intervals were either for 2-, 4-, or 12-h, depending on weather conditions.

**Herbicide Analyses.** The automated Thermal Desorption Unit (ATDU) Model V (Canadian Centre for Advanced Instrumentation, Saskatoon, SK) was interfaced to a Varian 3400 gas chromatograph equipped with a Thermionic Specific Detector. Desorption efficiencies and quantitation were similar to those described for the monitoring of triallate and trifluralin vapors in air (Cessna and Kerr, 1993). Volatile products adsorbed on the minitubes were desorbed directly onto the gas chromatographic column (held at 60 °C) by heating the minitubes at 240 °C and eluting with Ultra High Pure (UHP) helium at a flow rate of 6.5 mL min<sup>-1</sup> for 15 min. The GC column was a Hewlett-Packard HP-1 fused-silica, cross-linked capillary column 30 m × 0.53 mm i.d. with a 0.88  $\mu\text{m}$  film thickness of dimethylpolysiloxane. After the products were trapped, as described, on the GC column, the oven temperature was increased at a rate of 10 °C min<sup>-1</sup> from 60 to 240 °C and held at this temperature for 7 min. The Thermionic Specific Detector was maintained at 300 °C and operated at a bead current of 3.1–3.2 amps. The column gas was UHP helium at a flow rate of 6.5 mL min<sup>-1</sup> with column makeup gas of UHP nitrogen at 23.5 mL min<sup>-1</sup>. Detector gases were UHP hydrogen (4.5 mL min<sup>-1</sup>) and Ultra Zero air (175 mL min<sup>-1</sup>). Under these conditions, the retention times for ethalfuralin, trifluralin and triallate were 27.82, 28.02, and 29.50 min, respectively. These retention time values include the 15-min desorption period. Responses to all herbicides were linear over the range 0.3–100 ng with  $R^2$  values between 0.98 and 1.00. Typical GC chromatograms (background corrected) derived from standards and from air samples are shown in Figure 1.

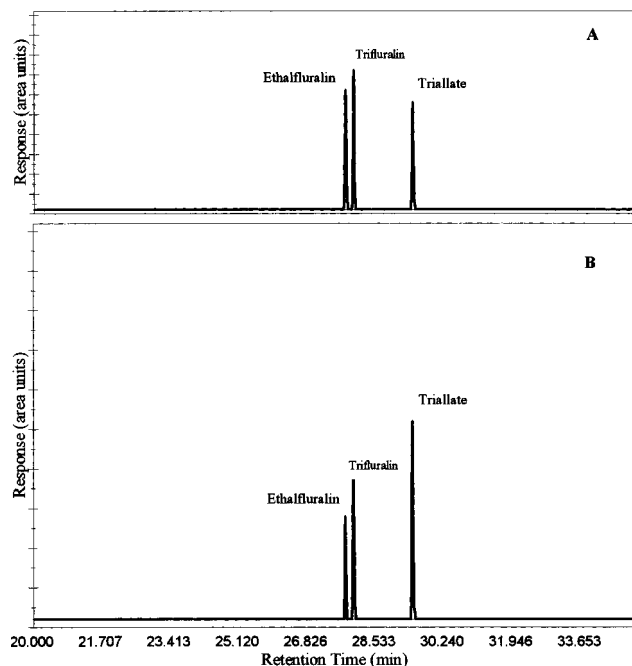
Thermal desorption efficiencies of triallate and trifluralin using this system are quantitative (Cessna and Kerr, 1993) and similar studies with ethalfuralin (data not shown) also confirmed quantitative desorption. Desorbed herbicides were quantified using minitubes fortified with known concentrations of the three herbicides as analytical standards.

A Varian Star Chromatography Work Station (Rev. 4.0) was used for instrument control and data integration. Concentrations of ethalfuralin, trifluralin, and triallate adsorbed by the various minitubes at the six heights at every sampling period were calculated and expressed as ng m<sup>-3</sup> of air sampled.

**Meteorological Data.** Windspeed and wet/dry-bulb temperature profiles were determined at the same heights as those of the air samplers using a six-level micrometeorological system as described (Shewchuk and Grover, 1981; Grover et al., 1985). A tipping bucket rain gauge measured rainfall. Wind sensors at the six heights were three-cup rotating miniature Rimco-Csiro anemometers. Micrometeorological data were collected continuously over the study period at 15-min intervals by a field-positioned data acquisition system (CR-10 datalogger, Campbell Scientific Inc., Edmonton, AB), interfaced to a computer via a short-haul modem.

Soil moisture determinations were made at 1000h every day by taking surface soil samples from the top 0.5 cm at four different field locations, with drying to constant weight at 80 °C.

**Vertical Flux Calculations.** The vertical pesticide mass flux ( $F$ ) from the field surface was calculated using the equation



**Figure 1.** Chromatograms (background corrected) of 6.3 ng of ethalfluralin, trifluralin, and triallate standards (A) and of desorbed herbicides (B) collected between 1600h and 1800h on Day 20 by the 50-cm height minitube.

$$F = K \Delta P / \Delta Z$$

where  $K$  is the turbulent eddy diffusivity coefficient and  $\Delta P / \Delta Z$  is the gradient of pesticide concentration (Parmelee et al., 1972; Shewchuk and Grover, 1981).

The turbulent diffusivity coefficients were determined from the corresponding profiles of the various meteorological parameters as described (Shewchuk and Grover, 1981; Grover et al., 1985) using the equation

$$K = \frac{k^2 \Delta U \Delta Z}{[\ln^2(Z_2/Z_1) \Phi^2]}$$

where  $k$  is the von Karman constant (0.41),  $\Delta U$  is the difference in wind speed at heights  $Z_2$  and  $Z_1$ ,  $\Delta Z$  is the difference in heights  $Z_2$  and  $Z_1$ , and  $\Phi$  is a stability correction factor (Shewchuk and Grover, 1981; Grover et al., 1985).

Turbulent eddy diffusivity coefficients were calculated for 2-h intervals using a computer program. Ethalfluralin, triallate, and trifluralin flux calculations were carried out for each 2-h sampling period. Herbicide fluxes for longer sampling periods were estimated by dividing these sampling times into 2-h intervals (Grover et al., 1988).

**Soil Residue Analysis.** These were conducted on 6 May 1996 prior to study commencement, and on 17 June 1996, three days after the second 5-cm soil incorporation. To determine amounts of ethalfluralin, trifluralin, and triallate in the field soil eight 7.62-cm i.d. by 10-cm soil cores (total surface area 365 cm<sup>2</sup>) were randomly sampled from four locations. The cores from each area were pooled, weighed (approximately 3 kg), mixed, subsampled, and analyzed as described (Grover et al., 1988). Aliquots (40 g) of the four mixed soils were analyzed by shaking for 1 h with extraction solution (100 mL) containing acetonitrile, water, and acetic acid (80:20:2.5). After shaking, the soil extracts were allowed to stand overnight before being shaken for an additional 1-h period. The extracts were centrifuged for 4 min at 2000g, and 25 mL of supernatant (equivalent to 10 g of soil) was shaken with 5% aqueous sodium carbonate (100 mL) and *n*-hexane (25 mL). The organic layer was dried over anhydrous sodium chloride (5 g) and examined for the three herbicides by adding 10  $\mu$ L to Tenax-TA resin minitubes. Quantitation was by thermal desorption gas chromatographic analysis, as described. Aqueous acidic acetonitrile, in conjunction with an

**Table 3.** Mean Daily Weather Parameters Measured at 1 m Height, and Surface Soil Moisture, for Study Period (28 May to 20 June 1996)

day	temperature (°C)		rain (mm)	humidity (%)	wind speed (m s <sup>-1</sup> )	surface 0.5 cm moisture at 1000h (%)
	max	min				
1	22.7	8.1	0.0	55	4.1	6.2 ± 0.6 <sup>a</sup>
2	19.6	3.7	0.4	77	4.4	5.5 ± 1.0
3	19.5	5.1	1.9	89	2.1	8.2 ± 0.5
4	21.8	2.2	0.0	75	1.5	14.1 ± 0.7
5	16.9	6.3	0.6	86	4.8	5.1 ± 0.5
6	18.1	5.9	0.0	88	4.6	9.7 ± 1.4
7	22.6	1.4	0.0	70	2.1	8.1 ± 0.8
8	26.0	12.0	7.4	82	3.9	38.9 ± 0.9
9	16.9	11.6	3.4	95	3.5	44.0 ± 0.8
10	22.9	6.8	0.0	81	2.0	30.6 ± 2.7
11	30.0	10.8	0.0	72	4.1	10.0 ± 0.4
12	34.2	10.8	0.0	71	3.6	11.5 ± 0.2
13	33.1	12.1	0.0	67	2.4	10.4 ± 1.9
14	27.5	14.2	0.6	74	3.6	7.9 ± 0.5
15	27.5	8.7	<0.1	80	3.0	13.2 ± 1.6
16	23.8	6.6	0.0	65	3.4	10.2 ± 0.9
17	29.2	9.4	1.7	70	3.6	9.3 ± 1.0
18	24.2	13.3	2.8	88	4.0	28.3 ± 1.4
19	23.3	8.2	0.0	80	2.3	19.8 ± 1.7
20	21.3	10.3	5.6	90	4.2	10.3 ± 1.1
21	29.8	13.8	6.6	83	7.3	22.4 ± 1.2
22	20.1	10.2	4.4	82	4.7	38.0 ± 4.0
23	20.6	7.9	0.0	77	5.7	23.4 ± 1.0
24	18.3	9.6	0.0	78	7.6	15.6 ± 1.3
mean	23.7	8.7				

<sup>a</sup> Mean and standard deviation from four replicates.

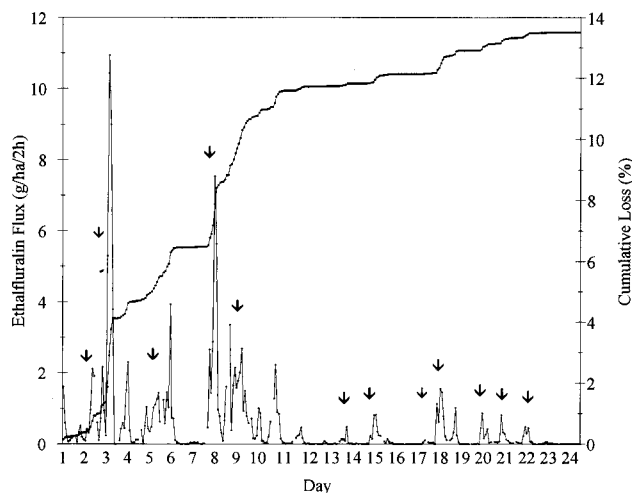
extended solvent extraction, has proven to be an excellent extractant for aged residues of ethalfluralin, trifluralin, and triallate from Saskatchewan field soils, including the present clay study soil (Hayden and Smith, 1980; Smith, 1992).

With the weight of the soil samples being based on an equivalent field area of 365 cm<sup>2</sup>, residues of all three herbicides remaining were calculated as kg ha<sup>-1</sup>.

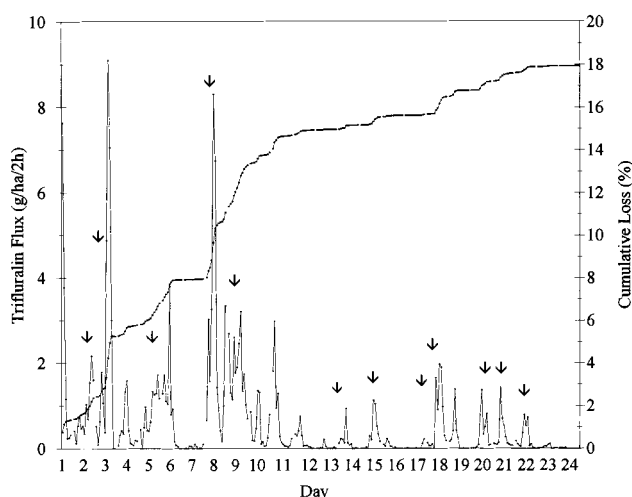
## RESULTS AND DISCUSSION

Weather conditions for the study period are summarized in Table 3. The mean maximum and minimum temperatures during the study period were comparable to those of the 30-year average. The 30-year average rainfall for the whole of June at the Regina Research Station is 72.6 mm on 12 occasions. During the study period, there was 35.4 mm of precipitation recorded on the 12 days when there were rainfall events. The majority of the rainfall (21.1 mm) was recorded (Table 3) between 13 and 18 June (days 17 to 22). On 4 and 5 June (days 8 and 9) 10.8 mm of rain was recorded. On the remaining five occasions rainfall was light.

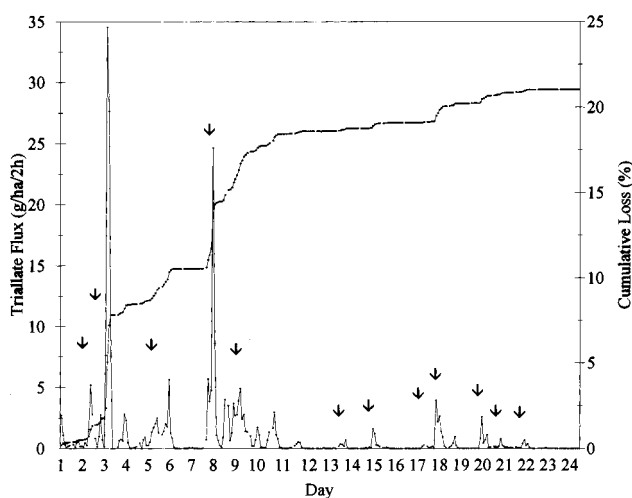
Flux calculations comparing the 2-hourly vapor losses of ethalfluralin, trifluralin, and triallate as g ha<sup>-1</sup>, as well as the cumulative loss as percent of applied, are summarized in Figures 2–4. Daily herbicide losses as g ha<sup>-1</sup> day<sup>-1</sup>, together with cumulative losses as percent of those applied are summarized in Table 4. Immediately following application, losses of ethalfluralin and triallate were less than 0.5%. Loss of trifluralin was greater, being 1.3% of that applied (Table 4). Major flux losses (Table 4; Figures 2–4) corresponded with precipitation events. Thus, following a light shower on day 2 there were immediate losses of approximately 1% of each chemical. Losses of approximately 3% for both dinitroanilines and 6% for triallate occurred after rain on day 3. Similarly, on days 5, 8, and 9 there were vapor losses immediately after a precipitation event.



**Figure 2.** Ethalfuralin fluxes ( $\text{g ha}^{-1} 2 \text{ h}^{-1}$ ) and cumulative vapor loss (% of applied) over the 24-day study. Arrows indicate rainfall events.



**Figure 3.** Trifluralin fluxes ( $\text{g ha}^{-1} 2 \text{ h}^{-1}$ ) and cumulative vapor loss (% of applied) over the 24-day study. Arrows indicate rainfall events.



**Figure 4.** Triallate fluxes ( $\text{g ha}^{-1} 2 \text{ h}^{-1}$ ) and cumulative vapor loss (% of applied) over the 24-day study. Arrows indicate rainfall events.

Further small losses were recorded on days 14, 15, 17, 18, 20, 21, and 22 following rain showers. Over the 24-day study period, 21% of applied triallate, 18% of the trifluralin, and 14% of the ethalfuralin volatilized from the surface.

**Table 4.** Daily and Cumulative Losses of Ethalfuralin, Trifluralin, and Triallate as Vapor from Treatment Area between 28 May (Day 1) and 20 June 1996

day <sup>a</sup>	ethalfuralin (1.06 kg a.i. ha <sup>-1</sup> )		trifluralin (0.99 kg a.i. ha <sup>-1</sup> )		triallate (1.28 kg a.i. ha <sup>-1</sup> )	
	g ha <sup>-1</sup> day <sup>-1</sup>	cumulative % of applied	g ha <sup>-1</sup> day <sup>-1</sup>	cumulative % of applied	g ha <sup>-1</sup> day <sup>-1</sup>	cumulative % of applied
1	2.8	0.3	13.4	1.3	4.7	0.4
2	7.3	0.9	10.2	2.4	12.3	1.3
3	33.8	4.1	28.5	5.3	83.0	7.8
4	6.1	4.7	5.2	5.8	8.2	8.5
5	8.7	5.5	10.2	6.8	12.1	9.4
6	9.9	6.4	11.0	7.9	14.3	10.5
7	0.3	6.5	0.4	8.0	0.3	10.5
8	25.1	8.8	30.9	11.1	55.3	14.9
9	19.4	10.7	21.9	13.3	31.4	17.3
10	4.2	11.1	5.8	13.9	7.4	17.9
11	5.6	11.6	8.0	14.7	7.0	18.4
12	1.4	11.7	2.4	14.9	1.9	18.6
13	0.2	11.7	0.3	15.0	0.1	18.6
14	1.0	11.8	2.0	15.2	1.9	18.8
15	2.9	12.1	3.7	15.5	3.8	19.1
16	0.4	12.1	0.7	15.6	0.3	19.1
17	0.2	12.2	0.4	15.6	0.5	19.1
18	6.1	12.7	8.3	16.5	11.9	20.0
19	1.9	12.9	2.9	16.8	2.0	20.2
20	2.3	13.1	4.1	17.2	5.9	20.7
21	2.0	13.3	3.8	17.6	2.2	20.8
22	1.8	13.5	3.0	17.9	2.2	21.0
23	0.2	13.5	0.4	17.9	0.1	21.0
24	0.1	13.5	0.1	17.9	0.0	21.0

<sup>a</sup> Rain was recorded on days 2 (0.4 mm), 3 (1.9 mm), 5 (0.6 mm), 8 (7.4 mm), 9 (3.4 mm), 14 (0.6 mm), 15 (<0.1 mm), 17 (1.7 mm), 18 (2.8 mm), 20 (5.6 mm), 21 (6.6 mm), and 22 (4.4).

All three herbicides have similar vapor pressures of the order of  $10^{-4}$  mmHg, and low water (25 °C) solubilities (Table 1). The latter are 0.3 mg L<sup>-1</sup> for both ethalfuralin and trifluralin and 4.0 mg L<sup>-1</sup> for triallate (Grover et al., 1988; WSSA, 1989). From these data, the soil water/air partition coefficients ( $K_{w/a}$ ) for ethalfuralin and trifluralin can be calculated to be 204 and 150, while the  $K_{w/a}$  for triallate is 1262. This would indicate a greater tendency for the two dinitroanilines to vaporize from soil water solution than triallate and to offset, to some extent, their greater soil adsorption which would tend to reduce their soil volatilities compared to that of triallate. Both ethalfuralin and trifluralin absorb in the ultraviolet (UV) region of the electromagnetic spectrum, so some photochemical decomposition on the soil surface or of their vapors in the air could have occurred during the study. This would not be the case with triallate which does not absorb in the UV region.

Volatility did not appear to be dependent on the soil surface temperature. On the days of greatest volatility, temperatures were relatively low (Tables 3 and 4). From laboratory studies, it has been noted (Smith, 1970) that negligible losses of triallate occurred from air-dried soils after heating at 50 °C for 28 days.

The mean daily windspeed varied from 1.5 to 7.6 m s<sup>-1</sup> and did not seem to be a major factor in the loss of herbicide vapors (Tables 3 and 4), since higher wind speeds did not result in greater fluxes. Similarly, high air humidity did not always result in higher herbicide fluxes (Tables 3 and 4). On days of rain, when the highest fluxes were recorded, the humidity varied between 70% and 95%. During days without precipitation (days 4, 6, 7, 10, 11, 12, 13, 16, 19, 23, and 24), herbicide fluxes (Table 4) were much lower even though air humidity, with the exception of days 13 and 16, were within the same range as on the days with rain (Table

3). Although correlated with rainfall, volatility losses were also time dependent (Table 4; Figures 2–4), with 11%, 8%, and 7% of the applied triallate, trifluralin, and ethalfluralin being volatilized after 7 days when there had been 2.9 mm of precipitation. During the second 7-day period, with 11.4 mm of rainfall, a further 8%, 7%, and 5%, respectively, of the applied triallate, trifluralin, and ethalfluralin was volatilized. After soil incorporation on days 15 and 18 and until the end of the study there was 21.1 mm of rain accompanied by small losses of all three herbicides (2%–3%, Table 4; Figures 2–4). With incorporation and the mixing of the surface soil to a depth of 5 cm a reduction in herbicide fluxes would be expected.

These general observations are similar to those noted (Grover et al., 1988) during a previous study conducted at the Regina location with soil-incorporated EC formulations of triallate and trifluralin. It was observed (Grover et al., 1988) that fluxes of both herbicides were highest during the first week after application and were also correlated with rainfall. Loss of triallate and trifluralin vapor from the incorporated EC formulations were 10% and 12% of the applied amounts after 7 days, 13% and 17% after 28 days, and 18% and 24%, respectively over the 67-day study period. Both triallate and trifluralin are strongly adsorbed to soil organic matter with reported (Grover et al., 1979)  $K_{OC}$  values on the Regina clay of 1409 and 5542. It was considered (Grover et al., 1988) that immediately after application of the EC formulation, both triallate and trifluralin were not sufficiently strongly adsorbed to the soil to prevent their volatilization. During the first week, an aging mechanism could have occurred during which the herbicides became more strongly adsorbed to the soil with a consequent reduction in losses by volatility. Although reactions that take place during aging are poorly understood, such mechanisms as increased adsorption to soil colloids and a diffusion into, or reaction with, humic colloids have been postulated (Chiba, 1969; Khan, 1973; Calderbank, 1989).

In the present study, the herbicide granules were small (<0.6 mm), and the action of rain and wind would cause the granules to move into the surface soil layer and into the trash cover. Thus, released triallate and trifluralin would become sorbed to soil and plant material and behave in a manner similar to that observed during the EC formulation study (Grover et al., 1988). A similar situation can be envisaged for ethalfluralin, a dinitroaniline herbicide whose structure closely resembles that of trifluralin. Ethalfluralin is known to be strongly adsorbed to soil colloids (WSSA, 1989).

On 17 June (day 21), three days after the second surface incorporation, four areas of the treated field were sampled to a depth of 10 cm, and ethalfluralin, trifluralin, and triallate remaining in the soil were determined gas chromatographically following solvent extraction. The data indicate (Table 2) that  $250 \pm 36$  g ha<sup>-1</sup>, or 24%  $\pm$  3% of the applied ethalfluralin, remained;  $373 \pm 64$  g ha<sup>-1</sup> trifluralin (38%  $\pm$  6%) and  $515 \pm 42$  g ha<sup>-1</sup> triallate (40%  $\pm$  3%) were also present. Thus, at the end of the study, 61%  $\pm$  3% of the applied triallate, 56%  $\pm$  6% of the trifluralin, and 38%  $\pm$  3% of the ethalfluralin can be accounted for as having volatilized and as still remaining in the soil. Unaccounted for residues were therefore about 40%–60% of those applied.

Two mechanisms could account for the missing residues: biological processes and photochemical losses

either in the air or on the soil surface. All three herbicides are known to be biologically degraded in the soil under favorable conditions. In the clay soil of the study, it has been reported that the field breakdowns of incorporated triallate and trifluralin are similar (Grover et al., 1988); while other field experiments indicate (Hayden and Smith, 1980) a similar breakdown rate of incorporated ethalfluralin and trifluralin in the clay. In the present study the granules were applied to the soil surface which is drier than the subsurface soil. At the time of herbicide application the soil surface was dry (Table 3). For the first seven days of the study, the soil surface moisture, determined at 1000h (Table 3), was less than the wilting point (20%), and biological activity would have been minimal for herbicide degradation. For the next three days the soil surface was moist and thus capable of sustaining biological breakdown. Thereafter, the surface moisture was below the wilting point until the first soil incorporation on 11 June (day 15). With incorporation into the moister subsurface soil there should have been sufficient biological activity to result in degradation of the three herbicides.

As mentioned above, dinitroaniline herbicides are known to undergo photochemical decomposition, and photochemical breakdown products in the air above fields treated with trifluralin have been detected (Probst et al., 1975, and references therein). However, quantitative losses of ethalfluralin and trifluralin as a result of photochemical processes under field conditions, both on the soil surface and as vapor in the atmosphere, remain to be assessed.

It was thus concluded that some of the unaccounted for herbicide residues were the result of biological and, also in the case of the two dinitroaniline compounds, photochemical losses, but no assessment regarding the relative contributions of the two mechanisms can be made. In addition, the experimental design may have led to the underestimation of the herbicide fluxes, since it has been reported (Grover et al., 1988) that the aerodynamic method, used for the calculation of volatilization of incorporated EC formulations of triallate and trifluralin, appeared to underestimate vapor losses of both herbicides.

From this study with granular formulations and delayed incorporation, it was concluded that volatility losses of ethalfluralin, triallate, and trifluralin do occur, but after soil incorporation such volatility losses are considerably reduced.

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