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Fate of 2,4-D *Iso*-octyl Ester after Application to a Wheat Field[1]

R. GROVER, S. R. SHEWCHUK, A. J. CESSNA, A. E. SMITH, AND J. H. HUNTER[2]

ABSTRACT

Dissipation of *iso*-octyl ester of 2,4-dichlorophenoxyacetic acid (2,4-D) and its acid metabolite in air, crop, and soil components were measured in a wheat (*Triticum aestivum* L.) field during and following application. Drift losses during application were only 0.2% of the amount applied. Air samples, collected at six heights ranging from 30 to 200 cm above the crop canopy during the first 7 d after application showed distinct ester gradients in the air, with concentration highest in the samples closest to the crop canopy. The highest concentration was measured during the afternoon of day 1 when 1604 ng m^{-1} were recorded 30 cm above the crop canopy. The vertical flux of the ester showed distinct diurnal variations with maxima reached in the early afternoon of day 1 and 2, followed by a rapid decline of the ester flux thereafter, corresponding with the depletion of the ester from the crop canopy. The total or cumulative vapor losses of the *iso*-octyl ester over the 5-d sampling period were estimated to be 93.5 g ha^{-1} or 20.8% of the amount applied.

The crop canopy intercepted 52% of the applied ester and acted as the major source of vapor losses. The magnitude of vapor activity was controlled primarily by the atmospheric stability and air temperature following application. On entry into the crop, the ester was hydrolyzed to the acid metabolite, which reached its maximum level on day 3. There appeared to be a rapid initial metabolism of the acid followed by a slow decline.

Ester losses from the soil surface occurred only when the soil surface was moist, i.e., after a rainfall event or in the early hours of the morning following the deposition of dew. In addition, both the hydrolysis of the ester and the subsequent degradation of its acid metabolite in the soil were dependent on the availability of surface soil moisture. No detectable 2,4-D remained in the soil after 34 d.

Additional Index Words: residues, soil, air, crop, herbicide vapor flux, application losses, postapplication losses.

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Monitoring of airborne residues, both in the Canadian prairies and elsewhere, has shown that the post application volatilization losses of herbicides play an important role in their dissipation in the environment (Farwell et al., 1976; Grover et al., 1976). Volatilization losses have been demonstrated on a quantitative basis for trifluralin (α,α,α-trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) and EPTC (*S*-ethyl dipropylthiocarbamate) where post-application losses by vapor activity were reported to be about 25 and 75%, respectively (White et al., 1977; Cliath et al., 1980). Quantitative documentation of actual losses under typical field conditions, especially where estimates of total volatilization losses along with herbicide dissipation in the crop and soil components, is minimal. Taylor et al. (1977) reported a rapid initial loss of two insecticides from the vegetation, followed by a slow dissipation, primarily from the soil. Most of the other studies measured pesticide fluxes under dryland field conditions, using soil-incorporated chemicals. Parmele et al. (1972) and Taylor et al. (1976) reported marked diurnal variations in maximum fluxes under generally moist soil conditions. Presumably, under these soil moisture conditions, the magnitude of flux was controlled by atmospheric stability, solar energy input, and volatilization of the pesticides at the solid-air interface. Harper et al. (1976) and White et al. (1977), on the other hand, showed that under dry soil surface moisture conditions, trifluralin and lindane (1,2,3,4,5,6-hexachlorocyclohexane) fluxes decreased to very low levels, even if atmospheric turbulence, soil temperature, and evaporative demand was high. These workers concluded that when the soil surface was not wet, pesticide fluxes appeared to be controlled by surface soil moisture content and the water content's effect on the adsorptive processes in the soil. This was further confirmed for a variety of pesticides, even when the pesticides were surface-applied (Glotfelty, 1981).

This paper reports the magnitude of 2,4-D (2,4-dichlorophenoxyacetic acid) *iso*-octyl ester losses by volatilization when applied as a postemergence treatment to a wheat (*Triticum aestivum* L.) field. In addition, the relative partitioning of the ester into the soil and crop components in the field and its subsequent dissipation from each of these compartments is also followed.

MATERIALS AND METHODS

Crop Seeding and Herbicide Application

The study area, located on the northeastern part of the Research Station, Agriculture Canada, Regina, had over-wintered as standing stubble during the winter of 1979-1980. In 1980, the field was summer-fallowed during which period it was disced, cultivated twice, and also rod-weeded. The top 5 cm of the Ap horizon of the soil (0.1 g kg^{-1} sand, 2.8 g kg^{-1} silt, 7.1 g kg^{-1} clay) had 0.31 g kg^{-1} organic matter and a pH of 7.7. On 1 May 1981, 3.7 ha of the field was seeded to wheat (*Triticum aestivum* L. var. Neepawa) at 100 kg ha^{-1} with a discer set at a depth of 7 cm and disc spacing of 18 cm. No fertilizer was applied. The wheat seedlings emerged on 14 May. On 25 June, when the wheat seedlings were 20 cm in height and had five leaves and two tillers, the field was sprayed with the *iso*-octyl ester of 2,4-D at a rate of 0.5 kg ha^{-1} (acid equivalent) between 0900 and 1000 h (CST), using a tractor-mounted sprayer. The sprayer boom, 7.4 m wide and fitted with 80° nozzles, was set at 58 cm above the ground to give a uniform coverage on the target plants at a 15-cm height. The sprayer was calibrated to deliver 100 L ha^{-1} of 2,4-D as an aqueous emulsion at 207 kPa while traveling at 5 km h^{-1}. The percent crop canopy coverage at time of herbicide application was 56 ± 7% ($P = 0.05$), as determined from field photographs using the point intercept method.

On-target deposits of the ester during application were determined by placing 12 glass petri dishes (140 mm diam or 0.0154 m^2 in area) on bare soil between crop rows (three dishes per quadrant). The petri dishes were covered immediately after the sprayer had passed over and stored until analysis.

Air Sampling

Air samples were collected at six heights downwind of the target area during application at a temporary sampling site (0900-1000 h CST). Immediately after application, all sampling and meteorological

[1] Contribution of Environmental Chemistry of Herbicides Section, Research Station, Agriculture Canada, Regina, SK S4P 3A2, Canada. Received 14 May 1984.

[2] Section head, meteorologist (Sask. Res. Council, Saskatoon, SK), residue chemist, residue chemist, and agronomist, respectively.

equipment was installed in the center of the field and subsequent sampling started at 1030 h CST. Air was sampled continuously, both day and night for the next 6 d, using a 2-h sampling interval. The location of the sampling mast in the center of the field ensured an adequate fetch length (about 100:1) for profile measurement. An air sampling system similar to that reported by Cliath et al. (1980) was employed in monitoring 2,4-D ester concentrations in the air. Samples were collected at the 30-, 50-, 75-, 100-, 150-, and 200-cm heights above the crop canopy. Each of the vapor traps, a 45-mm diam by 50-mm long polyurethane plug, was aspirated at 25 L min^{-1}. The trapping and extraction efficiencies of the foam plug for 2,4-D *iso*-octyl ester have been reported earlier (Grover and Kerr, 1981).

Calculation of Off-Target Drift during Application

Horizontal mass flow of the 2,4-D ester during the application period was calculated using both the mean horizontal wind speed and the herbicide concentration at each of the six heights downwind of the treated field, followed by the integration of the drifting cloud mass within the six sampling heights (Grover et al., 1978).

Vertical Flux Calculations

Herbicide flux calculations were carried out for each 2-h period for days 1 to 7, using two separate methods, the aerodynamic and energy balance methods (Parmele et al., 1972). The flux was determined as a product of the turbulent eddy diffusivity coefficient and the gradient of herbicide concentration (Parmele et al., 1972; Shewchuk and Grover, 1981).

The diffusivity coefficient is determined from profiles of various meteorological parameters. Windspeed, dry bulb temperature, and wet-bulb temperature profiles were determined in the atmosphere with a six level micrometeorological system (Shewchuk and Grover, 1981). Height measurements were taken starting at the top of the crop canopy and were spaced at intervals similar to the air samplers. Net radiation (Fritschen, 1965) was determined at the 1-m level and soil heat flux was measured with a heat flux plate, placed 10 mm below the soil surface. In addition, a profile of soil temperature was determined for depths of 2, 5, and 10 cm. A tipping bucket rain gauge and a potentiometric wind vane were used for rainfall amounts and wind direction, respectively.

Wind sensors were three cup rotating miniature anemometers (Bradley, 1969) fitted with a light-chopper type pulse generator and power amplifier circuit. The sensors of dry-bulb, wet-bulb, and soil temperature were thermistor networks. The wet and dry-bulb sensors were placed in a radiation shield and aspirated at 3 m s^{-1}.

All micrometeorological data were collected continuously over a 7-d period at 15-min intervals by a field-positioned data acquisition system. The eddy diffusivity coefficients, which ranged from 0.10 m^2 s^{-1} for daytime conditions to 0.01 m^2 s^{-1} for nighttime conditions, were calculated by a computer program for each 2-h sampling period that coincided with the times of collection for the herbicide samples. All profiles were corrected for the effects of stability. With the aerodynamic method, the zero plane displacement parameter was fixed at 0.7 times the height of the canopy (Monteith, 1973). The KEYPS (Sellers, 1969) function was the principle stability correction applied to the profiles. The determination of turbulent eddy diffusivity is based on the assumption that the vertical turbulent diffusion coefficients of both sensible heat flux and latent heat flux are similar. This similarity must be extended to herbicide flux as well.

The location of the towers was in the middle of the field and all instruments were placed within a 10-m diam plot. Field data were initially placed on ferric oxide tape cassettes and later transferred to a computer facility for calculation of herbicide flux.

Crop Sampling

The wheat field was divided into four approximately equal-sized quadrants for crop and soil sampling. Two composite samples of green wheat tissue were collected from each quadrant at the following times: before spraying and 1, 2, 3, 5, 9, 19, and 35 d after spraying. A composite sample consisted of 10 subsamples collected at random within a quadrant. Each subsample was cut at the soil surface from a 0.04 m^2 (20 by 20 cm) area. One set of composite samples was analyzed immediately after collection for 2,4-D *iso*-octyl ester residues, whereas the other set, reserved for total 2,4-D acid analysis, was chopped using a food cutter, placed in polyethylene freezer bags, and stored at −10°C until extraction.

A third set of composite crop samples was collected from each quadrant to establish a crop mass vs. sampling date curve. Each of these composite samples consisted of four subsamples, each 1 m^2 in size, collected at random within a quadrant. These composite samples were collected 7 d before spraying and on 14- and 21-d intervals thereafter. A regression curve, based on crop mass vs. time, was then established, which provided estimates of crop mass data for each of the herbicide residue sampling dates.

Soil Sampling

A check soil sample was taken 1 d prior to spraying, while soil samples were taken immediately after spraying on day 1, and on 2, 3, 5, 9, 19, and 34 d following crop spraying. From each quadrant of the field, six 7.5 cm i.d. by 7.5 cm soil cores (total surface area of 0.0265 m^2) were randomly sampled, usually on bare soil between the crop rows in the field to avoid cross contamination from the crop. The samples taken from each quadrant were pooled and separately stored in plastic bags. Immediately after collection, the soil samples were taken to the laboratory and weighed (approximately 2 kg) and poured through a Riffle Sampler® to divide the soil into two approximately equal parts. Each part was then separately and further divided by repouring through the Riffle Sampler® until there was about 100 g soil remaining. From each of the two reduced samples, representing duplicate subsamples from each of the field quadrants, 20-g portions were weighed into 125-mL glass-stoppered flasks, which were frozen at −10°C to await extraction and analysis. A moisture determination was carried out on the remaining soil from which the samples had been taken by heating 50 g of the field soils at 100°C for 24 h.

Analytical Procedures

EXTRACTION AND ANALYSIS OF AIR SAMPLES

Airborne residues of 2,4-D *iso*-octyl ester were soxhlet extracted from polyurethane foam plugs and analyzed gas chromatographically using a procedure described earlier (Grover and Kerr, 1981).

EXTRACTION, CLEANUP AND ANALYSIS OF ESTER IN THE CROP

A cylindrical sample washer (260 mm by 70 mm i.d.) was constructed from 18-gauge flat mesh expanded steel (3-mm hole), the bottom being attached with three pieces of copper wire. After the washing operation was complete, the bottom was removed and the wheat tissue pushed from the cylinder through the bottom end.

Each composite sample was weighed prior to analysis. All of the sample was then inserted into the cylindrical sample washer and immersed with occasional agitation in 1000-mL methylene chloride in a 2-L graduated cylinder for a period of 5 min.

The sample washer was then raised above the methylene chloride solution and the methylene chloride allowed to drain from the plant tissue. The plant tissue, while still in the sample washer, was rinsed with sufficient methylene chloride to return the volume in the graduated cylinder to 1000 mL. Fifty milliliters of the leaf surface wash was then transferred to a 100-mL RB flask and taken just to dryness using a rotary evaporator.

At later harvest dates, the sample holder was not large enough to hold an entire composite sample. The composite samples were then divided approximately in half, and each half was washed as described above, except that the second half was washed in the same 1000 mL methylene chloride as the first half of the sample.

Florisil® (4 mL, heated at 600°C for 48 h and deactivated with 5 mL water per 100 g Florisil®; Fisher Scientific) was added to 10 mL hexane in a 10 mm i.d. by 200 mm column, topped with 1 cm anhydrous sodium sulfate, and the hexane drained to the surface of the sodium sulfate. The residue in the 100-mL RB flask was transferred to the Florisil® cleanup column with two 1.5-mL hexane rinses of the RB flask. The column was then eluted with 27 mL of 5 mL acetone in 1 L hexane, the last 12 mL of which were concentrated using a rotary

evaporator and then taken to an appropriate volume with hexane for gas chromatographic analysis.

EXTRACTION, CLEANUP AND ANALYSIS OF TOTAL ACID IN THE CROP

The green wheat tissue was analyzed as described previously (Cessna, 1980) with the following modifications: 25 g green tissue was extracted and the combined decantates from centrifugation were taken to volume (250 mL) with water. Saturated NaCl (25 mL) was added to a 25 mL aliquot (equivalent to 5 g) and the procedure continued with all reagents and solvents decreased proportionally.

Methylation was carried out as described by Smith (1981) with the following modification: the cooled reaction mixture was extracted three times with 3 mL hexane, the hexane layer being transferred to a Florisil® cleanup column after each extraction. The Florisil® column, prepared as described for 2,4-D *iso*-octyl ester, was eluted with 38 mL of 5 mL acetone in 1 L hexane, the last 23 mL of which were concentrated with a rotary evaporator and taken to an appropriate volume with hexane for gas chromatographic analysis.

Following analysis, the concentrations of both the 2,4-D *iso*-octyl ester and total 2,4-D were calculated as mg kg^{-1} and then converted to g ha^{-1}, using the crop mass values (kg ha^{-1}) estimated from the 1 m^2 sampling regression curve. The amount of 2,4-D acid was calculated as the difference between the total 2,4-D and the amount of 2,4-D *iso*-octyl ester. At each sampling date, the mean amount of 2,4-D acid, total 2,4-D, and 2,4-D *iso*-octyl ester was calculated by averaging the data from each of the four quadrants.

EXTRACTION AND ANALYSIS OF ESTER AND ACID IN THE SOIL

All analyses were carried out within 4 d of collection by shaking each soil sample on a wrist-action shaker for 1 h with 50 mL of extraction solution containing acetonitrile, water, and glacial acetic acid (80:20:2.5 by volume). After centrifugation at 2000 × *g* for 4 min, 25 mL of supernatant were shaken with 100 mL of aqueous sodium carbonate solution (50 g L^{-1}) and 25 mL *n*-hexane in a 250-mL separatory funnel. After settling, the organic layer was examined gas chromatographically for the *iso*-octyl ester of 2,4-D. The aqueous phase was acidified by addition of 15 mL concentrated HCl and extracted with two 50 mL portions of diethyl ether. The pooled ether extracts were evaporated to dryness at 35°C using a rotary evaporator. Traces of water were removed from the flask by azeotropic distillation under reduced pressure following the addition of 10 mL benzene and 10 mL 2-propanol. The residue was quantitatively transferred, using ether, to a 50-mL glass tube from which the ether was evaporated using a stream of dry N_2. The residue containing any 2,4-D was methylated by adding 5 mL of boron trifluoride-methanol reagent (140 g kg^{-1}) as described earlier (Smith, 1981).

Recoveries of 2,4-D *iso*-octyl ester from four replicate samples of air-dried heavy clay, fortified at the 1.0 mg kg^{-1} level for 24 h prior to extraction, were all in excess of 95%. This indicated that no significant hydrolysis of the ester to the acid was occurring during extraction. Using aqueous acidic acetonitrile as extractant, the recovery of 2,4-D acid from the heavy clay is 90% (Smith, 1978).

Following analysis, the concentrations of both 2,4-D *iso*-octyl ester (as acid equivalent) and 2,4-D acid, per duplicate soil sample, were calculated and averaged for each quadrant. Since the weight of this soil was based on an area of 265 cm^2, amounts of 2,4-D remaining as either ester or acid could be determined as grams per hectare. At each sampling date, the mean concentrations of acid and ester forms of 2,4-D remaining were calculated by averaging the data obtained from the four quadrants.

Analysis of the check field soils taken 24 h prior to spraying showed that they contained < 10 g ha^{-1} of either the *iso*-octyl ester of 2,4-D (as acid equivalent) or of 2,4-D acid.

Gas Chromatographic Analysis

The gas chromatographs used were Tracor 560 or Hewlett-Packard 5700/5730A models, all equipped with ^{63}Ni electron-capture detectors. The glass columns (1.8 or 1.5 m by 4 mm i.d.) were packed with 100- to 120-mesh Ultrabond®-20M. Carrier gas was argon/methane (95:5), at flow rates of 30 to 40 mL min^{-1}. Depending on the carrier gas flow rate and the column length and temperature conditions, the retention times for the *iso*-octyl ester were 3.8 or 4.5 min and that for the methyl ester 3.5 and 3.8 min.

RESULTS AND DISCUSSION

Climatic Data

General weather conditions, including the soil moisture and soil temperature conditions at the test site, during the 7-d following the application of 2,4-D ester, are shown in Table 1. The 7 d were, in general, a dry period, except for a brief shower between 0100 and 0130 h on day 3. The dry conditions continued through the second week, the first major rainfall event occurring on day 18 when the field received 42.8 mm of precipitation. The wide fluctuations in the daily maximum and minimum air temperatures and relative humidity were typical for this area. The surface soil moisture levels showed a diurnal trend, with higher levels in the early part of the morning and the lower levels in the afternoon, the former no doubt due to dew deposition and capillary movement of soil moisture to the surface. The soil temperatures followed a diurnal trend as well with higher temperatures being recorded in midafternoon. It may be pointed out that the surface soil moisture conditions were, in general, near or below the wilting point level (0.2 kg kg^{-1}), except after a rainfall event.

Table 1. Climatic data and weather conditions on the test site during the first week of the study.

Date	Sample day	Rainfall†	Wind‡	Air temperature§		Soil				Relative humidity††		General weather conditions
						Moisture¶		Temperature#				
				0500	1500	0500	1500	0500	1500	0500	1500	
		mm	m s^{-1}	°C		kg kg^{-1}		°C		%		
25 June	1	–	2.6	–	23.4	0.167	0.068	–	30.8	–	65	Clear
26 June	2	–	4.9	8.5	28.3	0.123	0.058	13.0	27.5	90	67	Clear
27 June	3	3.8	3.9	15.5	22.6	0.412	0.140	16.2	31.0	86	68	Clear
28 June	4	–	2.7	9.3	20.3	0.151	0.088	13.0	24.2	94	65	Cloudy, 30%
29 June	5	–	3.6	4.2	24.0	0.130	0.060	10.6	26.4	98	57	Clear
30 June	6	–	4.0	11.8	29.3	0.094	–	14.2	26.0	90	60	Clear
1 July	7	–	3.4	13.3	26.1	–	–	15.0	–	94	–	Cloudy, 10%

† Major rainfall events (10 mm +) during the 35-d study period were day numbers 18, 23, and 35, which received 42.6, 12, and 11 mm of rainfall, respectively.
‡ Mean daily wind speed at 1-m height.
§ At 1-m height.
¶ Surface 1-mm samples taken daily at 0500 and 1500 h.
# Determined by extrapolation of soil temperature sensors to the surface.
†† Relative humidity at 1-m height.

Application Losses

The downwind 2,4-D ester mass drifting during application was calculated to be 0.2% of the amount applied. This is a horizontally moving mass and consists of droplet drift, vaporization from spray droplets, and volatilization of the ester from soil and crop surfaces during the application period of 1 h (0900–1000 h). The low drift losses are, no doubt, due to the selection of optimal operational and meteorological conditions for the spray operation. Maybank et al. (1978) have reported that droplet drift from ground rigs can be reduced to well below 1% by selecting appropriate conditions, such as nozzle angle, spray volume, pressure, wind speed, etc., as was the case in the present study. The vapor losses from the target area during application were also reduced to a minimum by spraying under favorable atmospheric stability conditions. An earlier study (Grover et al., 1973), which reported relatively high drift losses, was based on the application of a single swath (5 min), followed by a postapplication sampling for up to 90 min. In addition, the conditions under which spraying was carried out in the earlier study were most conducive to droplet as well as vapor losses.

Relative Concentrations of 2,4-D *Iso*-octyl Ester in Air, Crop, and Soil Components

Figure 1 presents vapor density profiles of 2,4-D *iso*-octyl ester every 2 h at 30-, 75-, and 150-cm heights during the first 24-h period, showing a distinct concentration gradient in the atmosphere, with the highest concentration in the samples nearest to the ground level. The gradients were maintained throughout the first 4 d of the study, after which they were not always discernible.

Unlike earlier work (Taylor et al., 1977; White et al., 1977; Glotfelty, 1981), the highest vapor densities of the herbicide were not encountered during or immediately following the spray application period (0900–1000 h). Instead, the peak concentration (1604 ng m^{-3}) was reached in the early afternoon of day 1 (1230–1430 h) at the 30-cm sampling height (Fig. 1), after which the concentrations in the air decreased rapidly, reaching a minimum level during 0230 to 0630 h on day 2. Concentrations of the ester in the air on day 2 again followed closely a diurnal pattern. This pattern is created by the daily solar cycle of heating and cooling, as established at the crop-soil-air interface.

During 0100 to 0130 h on day 3, there was a brief shower after which the concentration of 2,4-D ester in the air showed a pronounced increase (Fig. 1). For the rest of the sampling period, the peak concentrations of the ester were encountered mostly during the afternoons and were < 200 ng m^{-3}.

The concentrations of 2,4-D ester in the crop and the soil components also showed a rapid decrease in the first 2 d, after which there was a slow but continuous drop in concentration during the 7 d (Fig. 2). After the initial

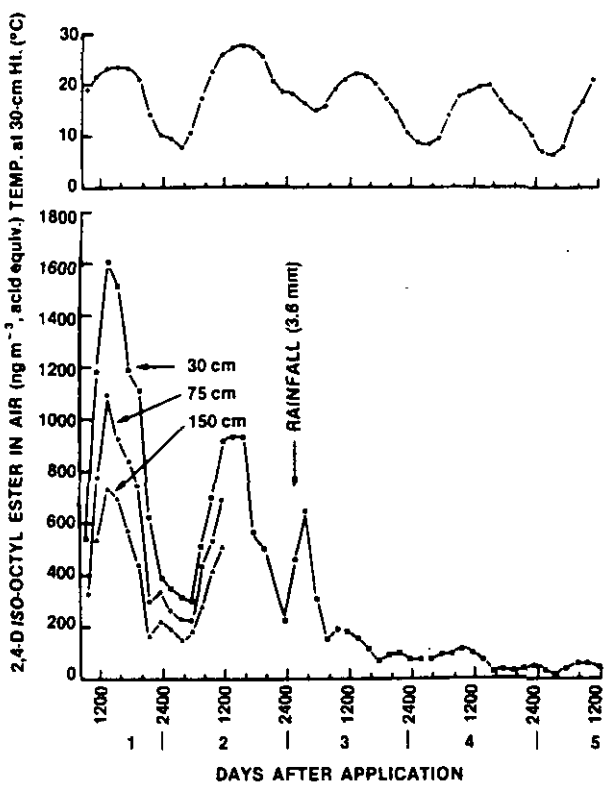

Fig. 1. Concentrations of 2,4-D *iso*-octyl ester in air at 30- [■), 75- (●), and 150- (▲) cm heights in air during first 24-h period and at 30-cm height thereafter and the corresponding air temperatures at 30-cm height after application.

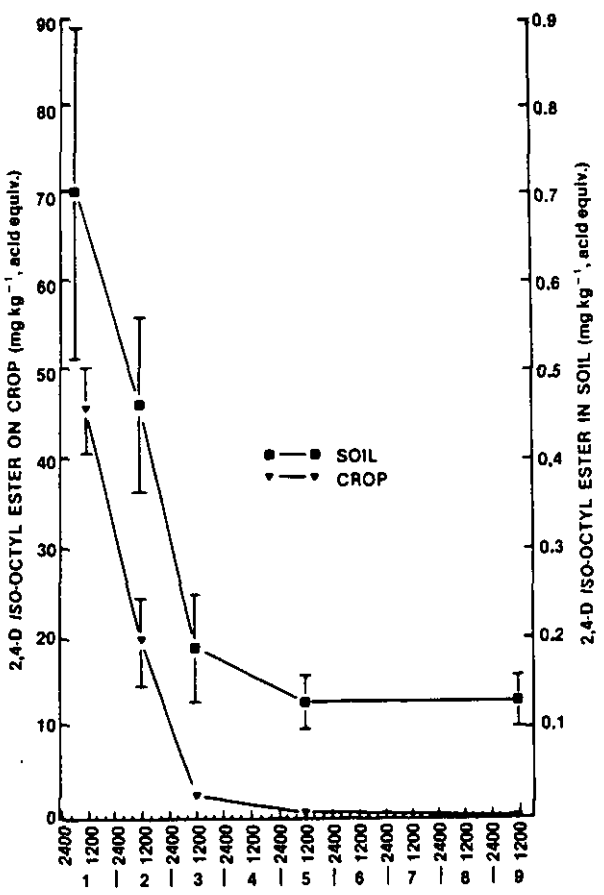

Fig. 2. Concentrations of 2,4-D *iso*-octyl ester in soil (0- to 7.5-cm depth) and in crop over the 9 d after application.

rapid decrease in the crop canopy from 45.4 to 2.7 mg kg^{-1} in the first 3 d, the ester concentration decreased further to 0.05 mg kg^{-1} in the crop by day 9. The initial deposits of the ester in the soil were calculated on a 0- to 1-mm and 0- to 7.5-cm depth basis, being thus 52.5 and 0.70 mg kg^{-1}, respectively. All subsequent calculations were carried out on a 0- to 7.5-cm depth basis only. The ester concentration in the soil decreased from 0.70 to 0.19 mg kg^{-1} in the first 2 d. Further decrease during the 7 d was slow, being down to only 0.13 mg kg^{-1} by day 9.

The initial surface concentrations of the *iso*-octyl ester on the crop and soil (1-mm depth basis) surfaces were quite comparable, being 45.5 and 52.5 mg kg^{-1}, respectively. The highest airborne residues in the field, however, were recorded 3 to 4 h after the initial application and were 1604 ng m^{-3} at the 30-cm height.

Vertical Vapor Flux of 2,4-D *iso*-octyl ester

Volatilization losses to the air for each 2-h sampling period (6 g ha^{-1} h^{-1}) and cumulative vapor losses to the air over the first 6 d after application (g ha^{-1}), using the herbicide concentration profile data and the corresponding micrometeorological measurements are presented in Fig. 3. The method for the determination of the turbulent eddy diffusivity coefficient for each sampling period was controlled by meteorological conditions. During light winds, the gradient as determined by the aerodynamic method, would vanish and during evening or sunrise-sunset conditions the energy balance method was of limited use. At most other times, however, there was good agreement between the two methods.

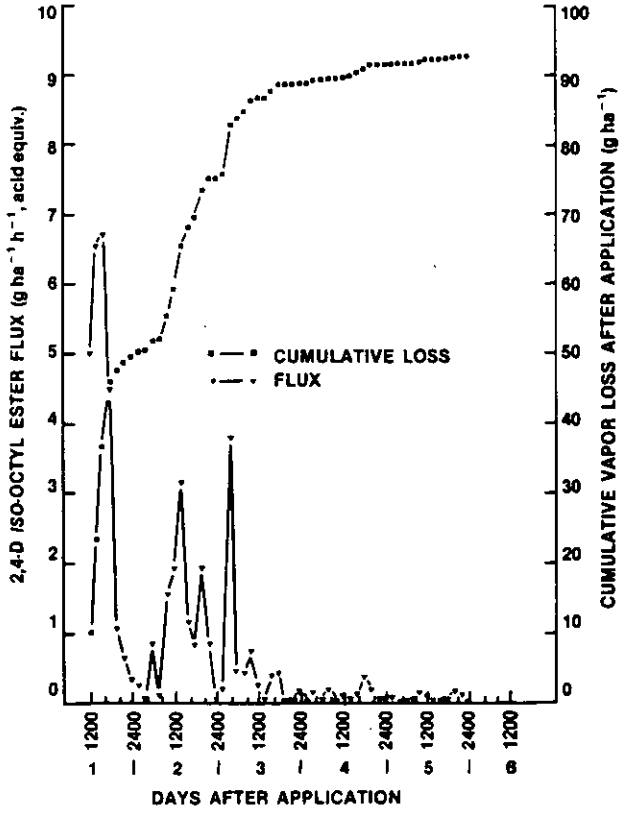

Fig. 3. Volatilization rate and cumulative losses of 2,4-D *iso*-octyl ester over 5 d after application.

Vapor flux of 2,4-D *iso*-octyl ester increased after application, reaching a maximum of 6.70 g ha^{-1} h^{-1} between 1430 and 1630 h, after which it declined rapidly to 0.04 g ha^{-1} h^{-1} between 0230 to 0430 h on day 2 (Fig. 3). There was a small, sharp increase in the ester flux between 0430 to 0630 h, followed by a steady increase in vaporization rate during day 2, reaching a maximum of 3.17 g ha^{-1} h^{-1} between 1230 to 1430 h. Following a brief rainfall event during the early hours of day 3 (0100–0130 h), there was a sharp increase in ester flux to 3.78 g ha^{-1} h^{-1} between 0230 and 0430 h. After this, distinct patterns in flux of 2,4-D *iso*-octyl ester were not clearly discernible. The pronounced diurnal variations in the maximum fluxes in the first 2 d following application were no doubt controlled in part by a diurnal cycle. The diurnal cycle influence on fluxes is reported by Parmele et al. (1972) and Taylor et al. (1976, 1977). In all these studies, the reported fluxes were either from vegetation or from relatively wet soils, where adsorptive influences can be minimal (Spencer et al., 1973). A primary factor in the diurnal influence is the solar cycle. Air temperature, no doubt, reflects not only atmospheric stability conditions but also the temperature environment of the volatilizing herbicide molecules. During the midafternoon periods when there is maximum solar heating, highly unstable atmospheres are created. In addition, maximum surface heating effects occur at the crop-soil-atmosphere interface due to direct solar energy absorption. Both turbulence, which is responsible for vertical transport of ester mass away from the canopy, and the surface heating effects enhance volatilization. During the evening when there is a sharp cutoff of the solar energy, the atmosphere becomes more stable and surface cooling effects become dominant, essentially suppressing the volatilization of ester deposits at the molecular level. Surface temperature is an extremely important factor in controlling volatilization. Several authors have shown that the vapor pressure and volatilization of 2,4-D esters are strongly dependent on temperature, including the range encountered under normal field conditions (Jensen and Schall, 1966; Flint et al., 1968; Hamaker and Kerlinger, 1969; Grover, 1975). Thus, the main factor controlling volatilization of the resident ester on the crop canopy to the air is likely the plant surface temperature, because it is influenced by solar radiation and turbulence.

In the present study, the ester was deposited on both the crop canopy and the soil surface, the latter being relatively dry (Table 1). It is well established that phenoxy ester losses from leaf surfaces can be substantial and after compensating for the amounts absorbed, can be similar to those lost from glass surfaces (Richardson, 1975; Que Hee and Sutherland, 1975). Vapor losses from dry soil, on the other hand, are minimal (Harper et al., 1976; Glotfelty, 1981). It is reasonable to assume, therefore, that the initial diurnal fluxes of the *iso*-octyl ester of 2,4-D were from the deposits on the crop canopy and not from the relatively dry soil surfaces in the present study. This hypothesis is further strengthened by the fact that there were little or no vapor fluxes of the ester once the ester had dissipated

Table 2. Cumulative losses of 2,4-D *iso*-octyl ester from volatilization.

Time, day	Cumulative amount volatilized as % of total	
	Applied	Volatilized
Application	0.2	0.9
1	11.2	53.9
2	16.9	81.1
3	19.9	95.8
4	20.5	98.5
5	20.8	100.0

from the crop canopy, whereas ester levels in the soil surface persisted for a considerable length of time thereafter (Fig. 2). The sudden vapor flux during the early hours of day 3, following a brief rainfall event can, however, be attributed to the release of the ester from the now wet soil surface, and was similar to those reported for trifluralin (Harper et al., 1976).

The total or cumulative loss of the *iso*-octyl ester over the first 5 d was estimated to be 93.5 g ha^{-1} or 20.8% of the amount applied (Table 2, Fig. 3). During the first 2 d, the cumulative pattern showed steep increases during the day, followed by leveling off during the night (Fig. 3), except during the early hours of day 3, where a sharp rise followed the rainfall event. Of the total amount of ester lost by volatilization, 53.9% was lost on day 1 alone, and this increased to 98.5% by day 4 (Table 2). It is important to note, however, that these losses were calculated mathematically using indirect methods, which no doubt are subject to potential errors, as was also pointed out by Parmele et al. (1972), Harper et al. (1976), White et al. (1977), and Glotfelty (1981), and Glotfelty et al. (1983). Thus, potential vapor losses of the 2,4-D *iso*-octyl ester will be different for different conditions, depending on factors such as atmospheric stability, temperature, and the amount of herbicide mass available for volatilization as well as soil moisture conditions and soil type.

Dissipation of Total 2,4-D and 2,4-D Acid in the Crop

The transformation of the crop residue data from mg kg^{-1} to g ha^{-1} corrected for the decline in concentration caused by crop growth. The crop canopy, which covered 56 ● 7% of area sprayed, intercepted 52% of the initial application (235 ● 32 g ha^{-1}). There was a rapid initial decline in total 2,4-D in the crop canopy to 85 ± 5 g ha^{-1} by day 3 followed by an extended slow decline, the total 2,4-D still being 44 ± 4 g ha^{-1} on day 35 (Fig. 4). This rapid initial decline was attributed in part to volatilization of 2,4-D *iso*-octyl ester from leaf surfaces (89 g ha^{-1} by day 3) and also to several other factors, as discussed below. The daily daylight vapor flux of the ester was directly proportional to the amount of ester deposited or remaining on the crop canopy and was best expressed by the equation:

$$y = ax$$

where

y = daily daylight vapor flux in g ha^{-1} d^{-1}

a = rate constant

x = residue of the ester on the crop canopy in g ha^{-1}

The value of the proportionality or rate constant a over the first 5 d was 0.179 ± 0.013 d^{-1}. Metabolism studies

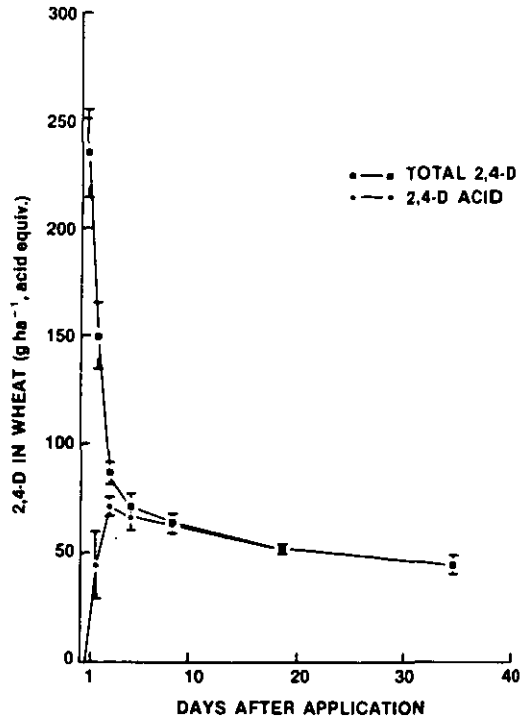

Fig. 4. Amounts of total 2,4-D (ester and acid) and acid alone in wheat over a 35-d period in the field.

concerning 2,4-D in wheat (Hallmen and Eliasson, 1972; Chkanikov et al., 1976) and wheat cell suspension cultures (Bristol et al., 1977) suggest that hydroxylation of the aromatic nucleus and side-chain degradation could account for significant losses of 2,4-D within a few days after application. In addition, photolysis of 2,4-D in droplets deposited on leaf surfaces (Crosby and Tutass, 1966) and possibly some washoff of 2,4-D acid and/or *iso*-octyl ester during the rainfall event on day 3 (Fig. 2) may have also contributed to the rapid initial decline of total 2,4-D in the crop canopy.

Although foliage samples on day 1 were collected over the period of 4 to 6 h after application, the total 2,4-D deposited on the crop canopy was not significantly different from the amount of 2,4-D *iso*-octyl ester found in the leaf wash. Thus, hydrolysis of the *iso*-octyl ester in wheat was much slower than that reported by Klingman et al. (1966) for the isomeric 2-ethylhexyl ester in Kentucky bluegrass (*Poa pratensis* L.). Hydrolysis of 2,4-D *iso*-octyl ester was evident by day 2, the concentration of 2,4-D acid being 39 ± 16 g ha^{-1} (Fig. 4). The concentration of 2,4-D acid increased to 71 ± 4 g ha^{-1} on day 3 and then decreased until approximating the total 2,4-D on day 9, when little or no *iso*-octyl ester was left on the crop canopy.

Dissipation of Total 2,4-D and 2,4-D Acid in the Soil

The average amount of total 2,4-D deposited during application on the bare soil between crop rows, as determined by the petri dish placement technique, was 450 ± 121 g ha^{-1}. The relative distribution of the ester between the crop canopy and the soil underneath the canopy can be inferred by subtraction of the initial crop

residue data from the petri dish data. Thus, the fraction of the herbicide reaching the soil under the crop canopy was estimated to be 215 g ha^{-1} or 48% of the application rate.

The dissipation of the ester and its acid metabolite were, however, monitored only in the bare soil between the crop rows. There was no change in the amount of total 2,4-D in the top 7.5 cm of soil on day 2, being 454 ± 76 g ha^{-1}, but it decreased to 316 ± 30 g ha^{-1} on day 3, following the rainfall event (Fig. 5). The total amount of 2,4-D decreased quite slowly over the next 14 d, being still not significantly different (239 ± 77 g ha^{-1}) on day 19. Following several rainfall events over the next 14 d, the total amount of 2,4-D was < 10 g ha^{-1} on day 34. It may be safe to assume that the behavior of 2,4-D ester and its acid metabolite in the soil directly under and within the crop canopy will be similar to that observed from samples collected from relatively bare spots.

The hydrolytic metabolite of the *iso*-octyl ester of 2,4-D, the acid, was observed in the soil on day 1 and its level was 156 ± 26 g ha^{-1} on day 2 (Fig. 5). The acid levels increased to 200 ± 41 g ha^{-1} on day 3 and remained between 185 and 210 g ha^{-1} over the next 14 d. Again, following several rainall events over the next 14 d, the 2,4-D acid concentration in the soil was < 10 g ha^{-1} on day 34. These results confirm earlier field plot work and laboratory studies that not only the initial hydrolysis of phenoxy esters to the acid forms, but also further breakdown of the acid metabolites were dependent on the availability of soil moisture (Smith, 1982).

CONCLUSIONS

1. The off-target drift losses during application were only 0.2% of the amount applied, indicating that if appropriate application parameters and weather conditions are selected, the drift during application can be reduced to well below 1% of the amount being applied.

2. Of the 450 g ha^{-1} of 2,4-D *iso*-octyl ester that was initially deposited on the target, 235 g ha^{-1} or 52% was intercepted by the crop canopy, all of it essentially still in the ester form, when sampled on day 1. It was assumed that the remaining 48% had infiltrated down to the soil under the crop canopy, since off-target losses during application were 0.2% of the amount applied.

3. The vertical vapor flux of the 2,4-D ester showed distinct diurnal variations with maxima reached in the early afternoon of both day 1 and 2. The major portion of the ester flux occurred during the first 2 d, followed by a rapid decline of the ester flux thereafter, corresponding to the depletion of 2,4-D ester from the crop canopy. The daily daylight cumulative vapor flux of the ester was directly proportional to the residues of the ester on the crop surfaces, being 17.9 ± 1.3% d^{-1} for the first 5 d. The total or cumulative vapor losses of the 2,4-D ester over the entire 5-d sampling period were estimated to be 93.5 g ha^{-1} or 20.8% of the amount applied. Thus postapplication vapor drift should be of major concern in areas where sensitive crops are grown.

4. There was a rapid decline of the total 2,4-D in the crop canopy, being only 36% of the initial deposition on the crop on day 3. This was followed by a slow but continuous decline, the total 2,4-D being still 19% on day

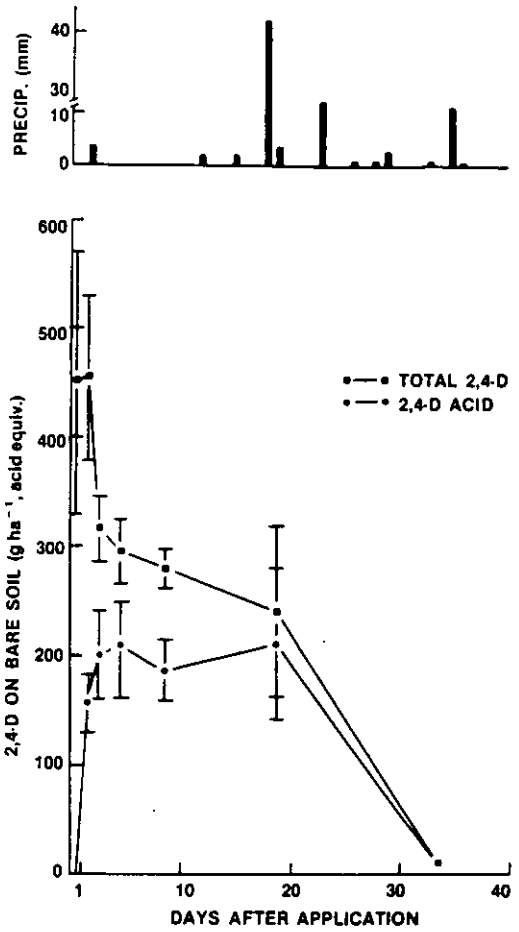

Fig. 5. Amounts of total 2,4-D (ester and acid) and acid alone in the top 0- to 7.5-cm soil layer over a 34-d period in the field.

35. Vapor losses of the ester accounted for only a part of the rapid initial losses. Presumably rapid metabolism of the acid in the crop, along with photolysis of the ester on the leaf surfaces and possibly some wash off following the rainfall event on day 3 may account for the remainder of the rapid initial losses.

5. As determined by the petri dish samplers and core samplers, the bare soil between the crop rows received the full application rate of 0.450 kg ha^{-1}. These bare areas were monitored for the dissipation of the ester and its acid metabolite during the growing season. The major ester vapor flux from the soil surface occurred during the early hours of day 3, following a rainfall event. Due to the prevalence of dry conditions over the next 14 d, the total 2,4-D in the bare soil had decreased only to 239 g ha^{-1} on day 19. However, following several rainfall events after day 19, the total amount of 2,4-D in the bare soil by day 34 was < 10 g ha^{-1}, the detection limit of the analytical method. Thus, vaporization of the ester from the soil surfaces and its hydrolysis to the acid metabolite and the subsequent degradation of the acid metabolite in the soil were all dependent on the availability of soil water.

6. 2,4-D acid, the initial hydrolytic metabolite of the ester in both the soil and the crop was detected in the samples collected immediately after application. The

acid metabolite increased rapidly, reaching a maximum over the next 2 d in both components. There was a slow but continuous decline of the acid in the crop over the next 30 d, presumably due to metabolism of the acid and/or conjugated forms of the acid. The acid metabolite in the soil did not degrade during the next 14 d of dry weather, but disappeared rapidly following a number of rainfall events by day 34.

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REFERENCES

Bradley, E. F. 1969. A small sensitive anemometer system for agricultural meteorology. Agric. Meteorol. 6:185–194.

Bristol, D. W., A. M. Ghanuni, and A. E. Oleson. 1977. Metabolism of 2,4-dichlorophenoxyacetic acid by wheat cell suspension cultures. J. Agric. Food Chem. 25:1308–1314.

Cessna, A. J. 1980. Simultaneous extraction and detection of residues of (2,4-dichlorophenoxy)acetic acid and bromoxynil from wheat. J. Agric. Food Chem. 28:1229–1232.

Chkanikov, D. I., A. M. Makeyev, N. N. Pavlova, L. V. Grygoryeva, V. P. Dubovoi, and O. V. Klimov. 1976. Variety of 2,4-D metabolic pathways in plants: Its significance in developing analytical methods for herbicide residues. Arch. Environ. Contam. Toxicol. 5:97–103.

Cliath, M. M., W. F. Spencer, W. J. Farmer, T. D. Shoup, and R. Grover. 1980. Volatilization of *S*-ethyl *N,N*-dipropylthiocarbamate from water and wet soil during and after flood irrigation of alfalfa field. J. Agric. Food Chem. 28:610–613.

Crosby, D. G., and H. O. Tutass. 1966. Photodecomposition of 2,4-dichlorophenoxyacetic acid. J. Agric. Food Chem. 14:596–599.

Farwell, S. O., E. Robinson, W. J. Powell, and D. F. Adams. 1976. Survey of airborne 2,4-D in south-central Washington. J. Air Pollut. Control Assoc. 26:244–230.

Flint, G. W., J. J. Alexander, and O. P. Funderburk. 1968. Vapor pressures of low-volatile esters of 2,4-D. Weed Sci. 16:541–544.

Fritschen, L. J. 1965. Miniature net radiometer improvement. J. Appl. Meteorol. 2:165–172.

Glotfelty, D. E. 1981. Atmospheric dispersion of pesticides from treated fields. Ph.D. diss. University of Maryland.

Glotfelty, D. E., A. W. Taylor, and W. H. Zoller. 1983. Atmospheric dispersion of vapors: Are molecular properties unimportant? Science 219:843–845.

Grover, R. 1975. A method for determining the volatility of herbicides. Weed Sci. 23:529–532.

Grover, R., and L. A. Kerr. 1981. Evaluation of polyurethane foam as a trapping medium for herbicide vapor in air monitoring and worker inhalation studies. J. Environ. Sci. Health Part B 16:59–66.

Grover, R., L. A. Kerr, J. Maybank, and K. Yoshida. 1978. Field measurement of droplet drift from ground sprayers. I. Sampling, analytical, and data integration techniques. Can. J. Plant Sci. 58: 611–622.

Grover, R., L. A. Kerr, K. Wallace, K. Yoshida, and J. Maybank. 1976. Residues of 2,4-D in air samples from Saskatchewan. 1966–1975. J. Environ. Sci. Health Part B 11:331–347.

Grover, R., J. Maybank, K. Yoshida, and J. R. Plimmer. 1973. Droplet and volatility drift hazards from pesticide application. Air Pollut. Control Assoc. preprint 73-106, Air Pollution Control Association, Pittsburgh, PA.

Hallmen, U., and L. Eliasson. 1972. Translocation and complex formation of picloram and 2,4-D in wheat seedlings. Physiol. Plant. 27:143–149.

Hamaker, J. W., and H. O. Kerlinger. 1969. Vapor pressure of pesticides. p. 39–54. *In* Pesticidal formulations research. Adv. Chem. Ser. no. 86. American Chemical Society, Washington, DC.

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.

Klingman, D. L., C. H. Gordon, G. Yip, and H. P. Burchfield. 1966. Residues in the forage and in milk from cows grazing forage treated with esters of 2,4-D. Weeds 14:164–167.

Jensen, D. J., and Schall. 1966. Determination of vapor pressures of some phenoxy herbicides by gas-chromatography. J. Agric. Food Chem. 14:123–126.

Maybank, J., K. Yoshida, and R. Grover. 1978. Spray drift from agricultural pesticide applications. J. Air Pollut. Control Assoc. 28: 1009–1014.

Monteith, J. L. 1973. Principles of environmental physics. American Elsevier Publishing Company, New York.

Parmele, L. A., E. R. Lemon, and A. W. Taylor. 1972. Micrometeorological measurement of pesticide vapor flux from bare soil and corn under field conditions. Water Air Soil Pollut. 1:433–451.

Que Hee, S. S., and R. G. Sutherland. 1975. Volatilization of butyl esters of 2,4-D from pyrex and leaves. Weed Sci. 23:119–126.

Richardson, R. G. 1975. Foliar penetration and translocation of 2,4,5-T in blackberry (*Rubus procerus* P.J. Muell). Weed Res. 15: 33–38.

Sellers, W. D. 1969. Physical climatology. University of Chicago Press, Chicago.

Shewchuk, S. R., and R. Grover. 1981. Description of a portable micrometeorological system to study pesticide volatilization and vapor transport. SRC Tech. Rep. 123, March. Saskatchewan Research Council, Saskatoon.

Smith, A. E. 1978. Relative persistence of di- and tri-chlorophenoxyalkanoic acid herbicides in Saskatchewan soils. Weed Res. 18: 275–279.

Smith, A. E. 1981. Relative persistence of MCPA, MCPB and mecroprop in Saskatchewan soils, and the identification of MCPA in MCPB-treated soils. Weed Res. 21:179–183.

Smith, A. E. 1982. Herbicides and the soil environment in Canada. Can. J. Soil Sci. 62:433–460.

Spencer, W. F., W. J. Farmer, and M. M. Cliath. 1973. Pesticide volatilization. Res. Rev. 49:1–47.

Taylor, A. W., D. E. Glotfelty, B. L. Glass, H. P. Freeman, and W. M. Edwards. 1976. Volatilization of dieldrin and heptachlor from a maize field. J. Agric. Food Chem. 24:625–631.

Taylor, A. W., D. E. Glotfelty, B. C. Turner, R. E. Silver, H. P. Freeman, and A. Weiss. 1977. Volatilization of dieldrin and heptachlor residues from field vegetation. J. Agric. Food Chem. 25:542–548.

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. 6:105–110.