Volatilization of Dieldrin and Heptachlor Residues from Field Vegetation

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Dieldrin and heptachlor were applied to a grass pasture at 5.6 kg/ha. Vapor density profiles up to 1 m height were measured up to 23 days after application, and vertical flux intensities were calculated using measured vapor density and wind speed profiles. Dieldrin (650 g/ha) and 2500 g/ha of heptachlor were volatilized from the target area during the first 12 h after application. Volatilization declined rapidly over the first 7 days. Soil and grass analyses confirmed that after 30 days 11% of the applied dieldrin and 4% of the heptachlor remained in the target area: 6% of the dieldrin and 2% of the heptachlor remained after 15 weeks. Marked diurnal variations in vertical flux intensities of both insecticides were observed during the initial periods of rapid volatilization.

In recent years post-application losses of pesticides by volatilization have been increasingly recognized as a pathway for general environmental contamination and as a process limiting their effectiveness. The physical chemistry of the problem has been reviewed in depth by Plimmer (1976) and the relevant aspects of the soil chemistry of pesticides have been discussed by Spencer et al. (1973) and Hamaker (1972). These reviews reveal that most investigators have concentrated on laboratory studies of pesticide vapor pressures and the way in which these are affected by soil adsorption or dissolution in water. Considerable attention has been devoted to studies of pesticide movement through soils and the extent to which volatilization rates are related to diffusion. Although some measurements of rates of insecticide volatilization from soils under field conditions have been published (Taylor et al., 1976; Willis et al., 1971, 1972), little or no data are available concerning rates of volatilization from exposed plant or vegetation surfaces in the field.

The work described here was designed to measure the volatilization of dieldrin and heptachlor, two chemically persistent insecticides, over a period of 3 weeks of warm summer weather after their application to field vegetation. The two insecticides were chosen to give data directly comparable with that from other studies in which they were incorporated to the 7.5 cm depth of surface soil (Taylor et al., 1976). Suitable techniques for measurement of their concentrations in the air over the treated field, together with the necessary analytical methods, were also available (Caro et al., 1971). The chemical stability of the two compounds also precluded uncertainties due to possible decomposition during the experiment.

Although not a typical crop to which either insecticide has been applied, an orchard-grass pasture was chosen as the experimental area. Measurement of the vertical flux intensities of pesticide vapor over the field required determination of the vertical eddy diffusion coefficients from micrometeorological observations (Parmele et al., 1972). In the present work, equipment limitations restricted these to measurements of wind profiles. These are most reliably interpreted over uniform stands of short crops which have a minimal response to fluctuations in wind speed (Lemon and Wright, 1969). Under these constraints, a uniform grass pasture, freshly mowed to 10 cm height, was chosen

as the best compromise to obtain data on the volatilization of the two pesticides from a treated vegetation surface.

EXPERIMENTAL SECTION

Experimental Site and Treatment. The site was a 3.34 ha rectangular field at the Agricultural Research Center at Beltsville, Md. The long (244 m) axis of the field was oriented in an east–west direction with a smooth 3% slope toward the northeast corner. The surrounding area consisted of other open fields to the north and south, and woodland approaching to about 15–20 m at both the east and west ends. The soil was fine sandy loam. The field had never received any previous applications of organochlorine insecticides.

On July 7, 1973, the existing stand of orchard grass (*Dactylis glomerata* L.) was mowed to a height of 10 cm and the clippings removed from the field. No further mowing or treatment, other than the insecticide application, was made during the whole experiment. Between 0930 and 1030 EDT, on July 12, dieldrin and heptachlor were applied together as a single uniform spray containing 5.6 kg/ha of both active dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo*,-*exo*-5,8-dimethanonaphthalene) and heptachlor (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene). The application was made with a regular farm spray rig equipped with a 21-ft spray boom mounted at about 70 cm height. Both were used as regular commercial formulations supplied by the Shell Chemical Company and Velsicol Corporation, respectively. The insecticides were applied to a rectangular 2.00 ha area (82 × 244 m) within the total experimental area, leaving untreated strips 27 m wide along the north and south boundaries as shown in Figure 1. These areas were left to ensure a smooth wind fetch over the boundary of the treated area without interference from fences or changes in vegetation height.

Air Sampling. On each sampling date, insecticide concentrations were measured at five heights (10, 20, 30, 50, and 100 cm) above the grass surface at two locations in the treated area, one in the center (point P_1, Figure 1) and the second on the downwind edge of the treated area: the location of the second was changed in response to wind direction. On July 12 (day 1), 2-h samples were taken from 1100 EDT (30 min after application) until 2300 EDT. On day 2 (7/13), samples were taken from 0400 to 1200 (noon) EDT. On days 3 (7/14), 6 (7/16), 9 (7/20), 14 (7/25), and 23 (8/3), samples were taken over daylight hours. Two-hour periods were used on days 3 and 6, and 4-h periods on days 9, 14, and 23.

Insecticide samples were taken by drawing air through 100 mL volumes of hexylene glycol in glass scrubbers mounted on masts. The outside of each scrubber was
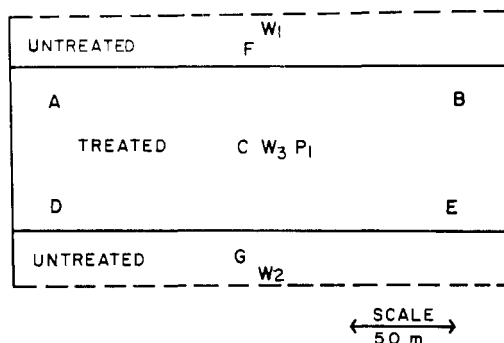
Figure 1. Dimensions of treated area and locations of sampling sites on the experimental field.

painted with reflecting aluminum paint to protect the sampling medium from light and reduce temperature variations. The exit of each scrubber was connected by rubber hose to a flowmeter leading into a surge tank exhausted by an electric vacuum pump. Flow rates, controlled by adjustable needle valves, were maintained at 8.3 L/min at all times. The vacuum pump was always placed on the ground several feet downwind from the sampling mast. At the end of each sampling period each scrubber was replaced with a new one containing fresh glycol. After removal from the scrubbers, samples were stored in the dark in glass bottles with close fitting Teflon-lined caps.

For analysis, the 100 mL volume of hexylene glycol was quantitatively transformed to a 2-L separatory funnel containing 1400 mL of 1% aqueous sodium chloride, and 100 mL of hexane was added. The mixture was shaken vigorously for 2 min. The layers were allowed to separate, and the aqueous layer was discarded. The hexane was brought to a convenient volume, concentrating with a Kuderna-Danish evaporative concentrator, where necessary, and a 3–8 μL aliquot was injected into a gas chromatograph equipped with a ^{63}Ni electron-capture detector. Owing to the large amounts of both insecticides present, no clean-up procedures were necessary to remove compounds interfering with dieldrin and heptachlor determinations.

Suitable gas chromatographic conditions were: column, glass, 165 cm $\times$ 2 mm filled with 1:1 10% DC-200 and 15% QF-1 on Gas-Chrom Q; temperatures, column, 220 °C; injector, 235 °C; detector, 310 °C; carrier gas, 95:5 argon:methane, flow rate 40 mL/min. Retention times under these conditions were: heptachlor, 3.0 min; dieldrin, 7.4 min.

Measurements on samples of hexylene glycol spiked with known amounts of both insecticides showed that recovery was quantitative. The detection limit of both heptachlor and dieldrin in air was approximately 0.1 ng/m^3.

Meteorological Observations. In order to calculate vertical flux intensities of insecticide from the observed gradients of vapor concentration, simultaneous observations were made of wind profiles over the treated area. Three masts, located at points W_1, W_2, and W_3 (Figure 1) carried recording anemometers mounted at 10, 50, 100, 150, 200, and 250 cm above the grass surface. Each anemometer measured total wind run over 30-min intervals.

Differential measurements of the air temperature (ΔT) were measured as a continuous record of the emf of a pair of ventilated thermocouples in shielded tubes at 20 and 50 cm heights, mounted on the central mast at W_3. From these, atmospheric stability corrections could be made. Continuous records of wind direction at the 3 m height were obtained from a wind vane mounted on the same

mast. The locations of all the meteorological equipment were unchanged throughout the experiment.

Measurements of daily temperature and humidity changes at the 120 cm (4 ft) height were made with a calibrated continuously recording hygrothermograph in a Stevenson screen at a regular climatological station located in similar terrain at a site 2 km west of the experimental field. The weather throughout the period was hot, hazy, and generally dry. Day temperatures ranged between 14 and 32 °C. Thunderstorms gave 12 mm of rain on day 10, 7.5 mm on day 11, and 30 mm on days 19 and 20; no runoff was observed from the treated area.

Grass and Soil Sampling and Analysis. Pesticide residues on the grass and underlying soil were measured at regular intervals up to 107 days after application. Samples were taken at five sites (A, B, C, D, E in Figure 1) within the treated area, and two sites (F and G) in the untreated boundary zones. At each sampling the grass at each site was clipped by hand to the ground within a 50 $\times$ 50 cm square template frame laid on the soil surface. The entire sample of vegetation within this frame was removed for analysis. Soil samples were then taken from within the clipped area by taking four cores to a depth of 7.5 cm using a 44 mm i.d. corer. Analysis of the entire sample of grass or soil thus permitted calculation of the amounts of pesticide residue per square meter of field surface. On successive samplings, the square template was placed about 30 cm east of the previous sample site so that the line of sampling points lay parallel to the direction traveled by the sprayer during the application.

Analytical procedures used for measurement of the insecticide residues in grass and soil have been described elsewhere (Caro, 1971; Freeman et al., 1975).

RESULTS

Insecticide Concentrations in Air. Table I contains the insecticide concentrations found in all the samplings on days 1 and 2. Selected data obtained on days 3 and 6 are presented in Table II. Marked gradients of insecticide concentration (vapor density) were observed at all times. In the first sampling after application, heptachlor concentrations were about five times higher than dieldrin, but this difference decreased as the general concentrations of both insecticides decreased during the experiment. In the afternoon hours of the third and sixth days, heptachlor concentrations were less than those of dieldrin.

Calculation of Insecticide Fluxes. The vertical flux intensities, or flux densities, were calculated from the vapor density gradients by the aerodynamic method using wind speed profile data obtained from the anemometer masts. The vertical flux intensity, $F\uparrow$, is given by the equation:

$$F = k^2 \frac{(C_1 - C_2)(U_2 - U_1)}{(\ln z_2/z_1)^2 \phi^2} \tag{1}$$

where C_1, C_2 and U_1, U_2 are the vapor densities and wind speeds, respectively, at heights z_1 and z_2 above the surface; k is von Karman's constant and is taken as 0.4. The stability correction term, φ, is introduced to take into account the effect of atmospheric stability on vertical diffusion. The form used was that developed by Pruitt et al. (1973), $\varphi = (1 - 16R_1)^{\pm 0.33}$, where R_1 is the Richardson number; the positive exponent was used for stable and the negative for unstable conditions as determined by the ΔT thermocouple measurements. This form of the stability correction term was developed for a surface similar to that in the present experiment.

The pesticide profile gradients were found by plotting the observed vapor densities against log $(z - z_0)$ and

Table I. Dieldrin and Heptachlor Concentrations ($\mu g/m^3$) at Sampling Heights between 10 and 100 cm over Orchard Grass on the First and Second Days after Spray Application

Day and sampling period (EDT)	Concentration, $\mu g/m^3$									
	Dieldrin					Heptachlor				
	Height above grass, cm									
	10	20	30	50	100	10	20	30	50	100
Day 1					$z_0 = 1.5$ cm					
1100-1300	61.2	60.0	41.4	33.0	21.2	311	277	211	171	109
1300-1500	46.3	42.2	40.1	32.0	23.5	148	124	117	92.7	60.5
1500-1700	32.2	31.6	26.1	20.9	13.9	64.1	57.8	49.5	34.8	26.5
1700-1900	18.9	14.3	17.4	11.3	9.1	29.5	23.4	24.3	18.1	12.3
1900-2100	9.1	7.60	5.6	5.6	2.9	18.7	14.4	10.6	8.9	4.3
2100-2300	4.5	3.9	2.6	1.8	1.4	15.6	10.4	7.8	5.0	3.3
Day 2					$z_0 = 1.5$ cm					
0400-0600	8.0	6.9	5.7	5.4	4.5	22.7	20.7	19.4	17.4	15.1
0600-0800	7.4	6.1	6.3	5.0	3.9	17.6	15.8	14.8	12.4	10.2
0800-1000	11.4	10.0	10.0	7.5	5.5	16.7	15.1	14.7	11.9	9.5
1000-1200	22.7	21.1	20.4	14.8	10.2	20.4	20.4	17.4	14.6	9.7

Table II. Dieldrin and Heptachlor Concentrations ($\mu g/m^3$) at Sampling Heights between 10 and 100 cm over Orchard Grass on the Third and Sixth Days after Spray Application

Day and sampling time (EDT)	Concentration, $\mu g/m^3$									
	Dieldrin					Heptachlor				
	Height above grass, cm									
	10	20	30	50	100	10	20	30	50	100
Day 3					$z_0 = 1.5$ cm					
0400-0600	6.3	5.6	3.4	2.0	1.3	9.0	8.6	5.2	2.6	1.4
0800-1000	14.0	12.3	10.4	7.8	5.0	8.0	6.6	5.8	4.6	3.2
1200-1400	27.7	27.4	22.4	18.3	11.5	12.2	10.9	9.3	7.0	4.9
1600-1800	18.5	18.2	15.7	16.3	10.0	8.6	8.2	6.9	6.5	4.8
2000-2200	11.9	9.8	8.1	6.3	2.9	9.3	8.1	6.5	4.6	1.9
Day 6					$z_0 = 1.5$ cm					
0400-0600	3.13	2.93	3.16	1.97	0.84	4.46	4.20	3.88	2.76	0.96
0800-1000		2.34	1.95	1.55	0.61		1.64	1.37	0.98	0.40
1200-1400	2.93	2.57	2.29	2.19	0.82	1.75	1.51	1.41	1.12	0.47
1600-1800	3.67	3.25	1.14	2.03	1.36	1.69	1.38	0.56	0.93	0.64
2000-2200	2.27	1.14	0.40	0.28	0.20	1.92	1.59	0.57	0.33	0.18

Figure 2. Vertical flux intensities of dieldrin and heptachlor during 2-h sampling periods on day 3.
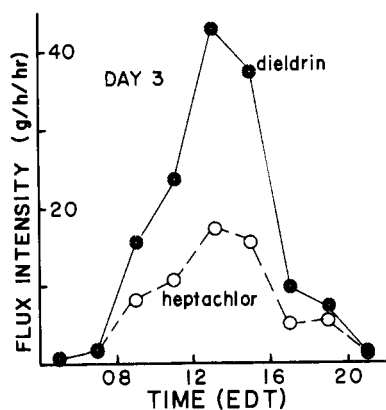

Figure 3. Vertical flux intensities of dieldrin and heptachlor during 2-h sampling periods on day 6.

drawing a straight line through the points. The pesticide vapor densities at the 20 and 50 cm heights used in the calculation were then taken from this line. The parameter z_0 is the "roughness length" determined from the wind profiles. Mathematically, it represents the height above the soil at which the wind speed extrapolated to zero on a plot of U against $\log z$. The values of U_1 and U_2 at the 20 and 50 cm heights were determined from the anemometer data in the same way. The vertical flux intensities calculated from eq 1 are therefore upward fluxes of insecticide through a horizontal plane 35 cm above the grass surface. Changes in grass height during the ex-
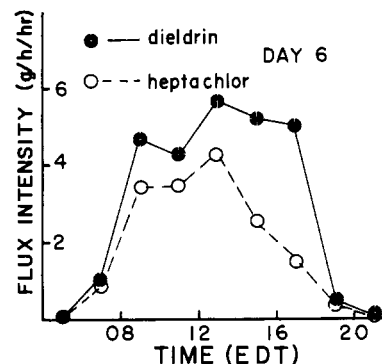
periment are presented in Table V.

Vertical flux intensities found during each sampling period on days 1, 2, 9, 14, and 23 are presented in Table III. Data for days 3 and 6 are plotted in Figures 2 and 3.

The most striking features of the data are the very high initial losses during the first few hours after application and the marked diurnal variations in flux intensity on subsequent days. Although the high initial volatilization decreased rapidly, becoming small in the late evening of the first day, 654 g/ha of dieldrin and 2554 g/ha of heptachlor were lost in the first 12 h after application. These represent 12 and 46% of the amounts initially

Table III. Hourly Vertical Flux Intensities (g ha^{-1} h^{-1}) of Dieldrin and Heptachlor from Orchard Grass

Day and sampling period	Hourly flux intensities, g ha^{-1} h^{-1}		Day and sampling period	Hourly flux intensities, g ha^{-1} h^{-1}	
	Dieldrin	Heptachlor		Dieldrin	Heptachlor
Day 1			Day 9		
1100–1300	169	822	0600–1000	2.13	1.95
1300–1500	80.4	296	1000–1400	4.22	2.22
1500–1700	60.6	128	1400–1800	3.00	1.35
1700–1900	16.2	29.4	1800–2200	0.62	0.50
1900–2100	0.6	1.4	Day 14		
2100–2300	0.2	0.6	0600–1000	0.70	0.67
Day 2			1000–1400	0.91	0.62
0400–0600	0.52	1.15	1400–1800	0.60	0.32
0600–0800	0.52	1.15	1800–2200	0.09	0.13
0800–1000	9.54	12.5	Day 23		
1000–1200	38.2	35.5	0600–1000	0.49	0.61
			1000–1400	0.59	0.63
			1400–1800	0.43	0.57
			1800–2200	0.04	0.05

Table IV. Observed Daily Volatilization Losses of Dieldrin and Heptachlor (g ha^{-1} day^{-1})

	Daily losses by volatilization, g ha^{-1} day^{-1}	
Day	Dieldrin	Heptachlor
1	654	2554
2	(325)[a]	(335)[a]
3	282	132
6	53.7	33.5
9	40.0	24.1
14	9.2	6.9
23	6.2	7.4

[a] Estimates assuming loss between 0400 and 1200 EDT is 30% of total.

applied to the field. Volatilization rates again increased rapidly after 0800 EDT on day 2. Unfortunately, sampling was discontinued before the peak rate was reached, but the increase clearly parallels that of the marked diurnal patterns evident on days 3 and 6.

The total quantities of pesticides lost by volatilization on each sampling day are presented in Table IV. These results were obtained by integration of the hourly flux values with the assumption that volatilization was small and could be neglected before 0600 and after 2200–2300 EDT. This assumption is supported by the data in Figures 2 and 3. Estimates for the second day assumed that the observed loss of 97.5 g of dieldrin and 100.6 g of heptachlor between 0400 and 1200 EDT was 30% of the loss for the

whole day, as found on the third day.

Residues on Grass and Soil. The residues found in the grass and soil samples are presented in Table V. These data, in mg/m^2, are the means of the five sites. The standard errors of the means are included. Considerable variations were found between individual sites due to uneven deposition of the insecticides on the grass. The range of this variation was similar to that found in earlier studies (Taylor et al., 1971). The dieldrin and heptachlor residues on the grass decreased rapidly over the first week, with a subsequent slower decrease. Although regression analysis showed that the decreases could be approximated by a logarithmic curve of the form log $[R] = A - bT$, graphical inspection suggested that the results could be best interpreted in terms of two separate equations, one describing the rapid and a second the slower loss. The equations, presented in Table V, indicate that over the first 5 days the dieldrin residues had an average half-life of 2.7 days and the heptachlor 1.7 days, or alternatively, 23% of the remaining dieldrin and 34% of the heptachlor was lost each day. Comparison of these figures with the volatilization data in Table IV shows that the losses can be fully accounted for by this pathway and there is no need to invoke any other mechanism to account for the decrease. Similar conclusions were reached by Harrison et al. (1967) in studies of the disappearance of dieldrin and other insecticides from apple trees in southeastern England and by Dekker et al. (1970) working with fruit trees and legume crops in Illinois. Harrison also observed an initial rapid

Table V. Pesticide Residues (mg/m^2 of Field Surface) on Orchard Grass and Underlying Soil for 107 Days after Application[a]

Sampling, days after application	Grass height, cm	Insecticide residues, mg/m^2					
		Dieldrin		Heptachlor		Heptachlor epoxide	
		Grass	Soil	Grass	Soil	Grass	Soil
0.12	10	154 ± 25	36 ± 10	71 ± 18	32 ± 10	0	0
2.0	10	99 ± 35	41 ± 9	23 ± 10	31 ± 8	0.5	0
5.1	22	42 ± 9	39 ± 7	8.5 ± 3	30 ± 7	0.9	0
8.0	23	29 ± 4	37 ± 15	4.5 ± 1	23 ± 4		0
22	27	34 ± 3	47 ± 9	3.6 ± 0.9	27 ± 7	1.8	2.8
35	30	14 ± 2	43 ± 5	1.2 ± 0.2	21 ± 5	0.9	3.0
55	30	12 ± 2	25 ± 6	1.0 ± 0.3	11 ± 2.0	0.8	3.0
79	30	7.7 ± 1.0	42 ± 7	0.4 ± 0.05	13 ± 2.5	0.6	6.1
107	30	5.9 ± 1.2	38 ± 6	0.25 ± 0.10	9.0 ± 2		5.9

Regressions of grass residues with time					
Period, days	Dieldrin	(r)	Heptachlor		(r)
0–5	log D = 2.21 − 0.11T	0.995	log H = 1.81 − 0.18T		0.984
5–107	log D = 1.58 − 0.008T	0.96	log H = 0.82 − 0.015T		0.97

[a] All data mean of five samples; ± values are standard errors of means.

decline in dieldrin residues with a half-life of between 2.5 and 4 days, followed by further volatilization at a declining rate.

Heptachlor epoxide residues on the grass showed a maximum on the 22nd day, but increased continuously on the soil after this time. The pattern of the observation suggests that the epoxide was volatilized from the grass, together with the parent heptachlor, but the accumulation of epoxide in the soil was due to the conversion of more persistent soil residues of parent heptachlor. No heptachlor epoxide was detected in the air samples.

Grass samples taken from site F in the untreated area upwind from the application contained 0.5 mg/m^2 of dieldrin and 0.2 mg/m^2 of heptachlor on the initial sampling. These figures are less than 0.5% of those in the treated area. Samples from site G in the downwind untreated area contained about 1.5 mg/m^2 of both insecticides. The dieldrin content of samples from sites F and G declined to less than 0.2 μg/m^2 after 80 days. Heptachlor was not detectable in them after 1 week.

Significant amounts of photodieldrin were found in air and grass samples after the first day. These results are discussed at length by Turner et al. (1977).

DISCUSSION

Initial Residues and Volatilization Rates. The data in Table III show that the volatilization rates immediately after application were very large, about 2000 g/ha of heptachlor, or 40% of the nominal application, being lost in the first 4 h. Since the data are 2-h means of rates that were changing rapidly, extrapolation to the initial value must be very approximate, but 600 g/ha of heptachlor and over 100 g/ha of dieldrin may have been lost before air sampling began at 1100 EDT. The first grass and soil samples were taken between 1300 and 1400 EDT. Since this was also a period of rapid volatilization and the times at which individual samples were taken were not recorded, reconciliation of the volatilization rates and grass residues is not possible for the first day. No precise estimate of the amount of the two insecticides that was lost by drift or evaporation of particles during spraying is possible. Since the evaporation was continuous from the time the formulation left the spray boom, any attempt to separate the rates of evaporation of the droplets in the air from those deposited on the grass is artificial, and the process is better regarded as a continuous, rapid, and highly dynamic system. If, however, the above observed and estimated volatilization rates up to 1300 EDT are taken together with the grass and soil data in Table V, about 40% of the dieldrin and 58% of the heptachlor applied can be accounted for as being in or having evaporated from the target area, the remainder being lost directly to the atmosphere as vapor or spray drops that never reached the target area. The weather during spray application was sunny with an air temperature of 20 °C (RH 40%) and a wind speed of 4.2 m/s (9 mph) at 2 m height, conditions favoring rapid evaporation of spray drops. The small amounts of residues in the samples from site G, in the untreated area 13 m from the downwind edge of the treated plot, showed that only small amounts were deposited on the grass outside the treated area: the bulk of the insecticides that did not reach the target area therefore appears to have been injected into the atmosphere by evaporation of spray droplets. In similar experiments in 1968 (Caro and Taylor, 1971), a sample of surface soil taken 50 ft from the downwind edge of an area treated with dieldrin using similar equipment was found to contain 0.02 ppm of dieldrin in contrast to concentrations between 4 and 8 ppm within the treated area.

Diurnal Changes in Volatilization. The data presented in Figures 2 and 3 show a marked diurnal change in vertical flux intensity (or volatilization) of both insecticides. The data for day 9 (Table III) also show the same effect, but the pattern is less evident on days 14 and 23, when the volatilization had fallen considerably. The results for day 2 (Table III) also show a marked increase over the morning hours until sampling was discontinued at noon.

Similar diurnal variations have also been reported in the volatilization of heptachlor and dieldrin residues incorporated into surface soil (Taylor et al., 1976). In the earlier work the diurnal variation was attributed to changes in water movement to the soil surface controlled by surface water evaporation—the "wick effect". In the present experiments the residues remained on the exposed plant and soil surfaces, and this mechanism cannot apply. Regression analyses show the flux intensities are about equally well correlated with several meteorological variables measured over the same sampling periods, including air temperature, temperature lapse, and wind speed at 1 m height. In a discussion of factors controlling rates of gaseous exchange between crops and the atmosphere, Lemon (1969) noted the large number of interlocking relationships existing between the conditions within a crop and those in the adjacent atmosphere, both sets of conditions being linked together by a complex of feedback mechanisms. Under these circumstances it is pointless to select one variable as the controlling factor, and it must be concluded that the diurnal variation in pesticide flux intensity is a direct result of the diurnal variation in solar radiation input affecting all other parameters.

This conclusion is confirmed by the vapor concentration data presented in Table II. If volatilization from the leaf surfaces were continuous over the 24-h period, very steep vapor density profiles would be expected close to the ground in the morning and evening when dispersion by turbulent mixing decreased and the vertical flux intensity became small. The conditions under which such gradients could have developed, characterized by temperature inversions giving a positive Richardson number, were encountered up to 0800 EDT and on the evenings of both days 3 and 6. No marked increases in vapor density gradients close to the ground were observed at any of these times, indicating that evaporation of the insecticides from the leaves ceased or was greatly reduced with decreasing solar energy supply. Calculation of the "residence time" of the insecticides, defined as the quantity of insecticide vapor in the air up to 1 m divided by the vertical flux intensity, gave values increasing from 8 s when flux intensities were highest at midday to about 10 min in the morning and evening. If the flux intensities were controlled solely by the rate of turbulent mixing, much larger values would be expected under stable atmospheric conditions when turbulence was low.

The vapor densities of both insecticides close to the grass surface can be estimated by extrapolation of the values in Tables I and II to zero height. Since the grass temperature was not measured, relative vapor densities (analagous to relative humidity) cannot be calculated, but they can be estimated from the climatological station temperature data. Such estimates indicate that the relative vapor density of dieldrin within the grass was close to 100% until 1300 EDT on the first day, when the air temperature was between 21 and 22 °C. According to Spencer and Cliath (1969), the saturation vapor densities at these temperatures are 64 and 74 μg/m^3, respectively. After the first sampling period, the relative vapor density decreased rapidly, falling

to 10% by late evening. Estimated values reached 30–40% during periods of rapid flux on the second and 20–25% on the third days. Lowest values were always found in the evening and early morning.

Relative vapor densities of heptachlor were much lower. Equilibrium vapor pressure data given by Bowery (1964) and Martin (1971) indicate that the saturation vapor density is about 54 times that of dieldrin at the same temperature. The estimated relative vapor density of heptachlor within the grass before 1300 EDT on the first day was thus 12% or less and remained much lower than that of dieldrin throughout the experiment. The results suggest that volatilization rates of pesticides in the field cannot be predicted in detail from their saturation vapor pressures. Although saturation conditions may be established close to the source for short-time periods after application, the amounts lost to the atmosphere will be governed by dispersion in turbulent flow. Variations in the latter will control the loss rate which will then reflect changes in solar energy input except where turbulence is imposed by strong winds. When saturation conditions are not present at the surface the rate of vapor formation will be directly controlled by the rate of energy input to the condensed phase. Thus, over time periods of about 1 day, volatilization rates will vary with changes in the energy input to the overall system. Over periods of several days or more the rate is principally controlled by the distribution of residues on the plant surfaces, decreasing as the fraction of surface covered by them is reduced or as they become adsorbed within the subsurface layers of plant tissue.

Long Term Changes in Volatilization. Tables IV and V show that the volatilization fell as the grass and soil residues decreased, but statistical and graphical analyses did not reveal any simple relationships. Both sets of data showed erratic variations. In the grass and soil these reflected sampling variability; in the volatilization data they were due to weather. Over the first 6 days the average daily loss by volatilization corresponded approximately to the decreases in residues on the grass, but no reconciliation of the two sets of observations was possible between the 6th and 23rd days owing to the variability of the grass data. The results suggest that after about the 6th day the soil residues became increasingly important in controlling the volatilization. Since the vapor pressure of the insecticides over the soil is very sensitive to the soil moisture content (Spencer et al., 1969) the volatilization would then no longer be directly related to the amount of pesticide on the soil, but would be greatly influenced by the soil moisture content. In field measurements of the volatilization of dieldrin applied to the surface of Commerce silty clay loam soil, Willis et al. (1972) demonstrated that, for several weeks after the application, losses were increased from less than 20 to over 100 g/ha^{-1} day^{-1} by maintaining the soil moisture in the 0.3 to 1 bar tension range. This dependence upon soil moisture makes extrapolation of the volatilization data beyond the 23rd day of the present experiment very uncertain. Estimates of the total post-application losses up to the 23rd day were, however, made by interpolation of the data of Table IV. This gave estimates of dieldrin loss as 1900 ± 250 g/ha, of which about 35% was lost on the first day and 90% in the first 7 days. The heptachlor estimates for the 23-day period were 3200 ± 250 g/ha, with 75% of this on the first day and 95% in the first week.

The best estimate of longer term losses was obtained from the grass and soil data of Table V. This indicates that about 130 g/ha of both insecticides were lost between the 35th and 107th days. This corresponds to an average of about 1.8 g ha^{-1} day, probably controlled by volatilization from the soil. Somewhat higher figures were reported by Willis et at. (1972), but the residues present in the surface soils of their experiments were between two and three orders of magnitude greater than those of the experiments reported here.

SUMMARY

Direct measurements of the volatilization of dieldrin and heptachlor applied to exposed field vegetation (orchard grass) at 5.6 kg/ha in sunny weather with air temperatures between 14 and 23 °C showed rapid losses with initial rates of 650 g/ha of dieldrin and 2500 g/ha of heptachlor on the first day. Over the first 5 days the average half-life of the dieldrin residues was 2.7 days and the heptachlor 1.7 days.

The volatilization rate declined sharply after the first week. Plant and soil analyses showed that 30 days after application about 11% of the applied dieldrin and 4% of the heptachlor remained in the target area. After 15 weeks the respective figures were 6 and 2% with almost all the residues on the soil. Small amounts of heptachlor epoxide were found on both soil and vegetation.

The decreases in residues on soil and grass could be entirely accounted for by volatilization. No runoff losses occurred and no evidence of rapid chemical degradation was found.

Marked diurnal variations were observed in the volatilization of both insecticides during the period of greatest loss early in the experiment, the rates closely following the diurnal variation in solar radiation. Flux intensities were controlled by the rate of evaporation from plant surfaces. Dispersion by turbulent diffusion was never limiting. As overall volatilization decreased due to depletion of the residues remaining on plant surfaces, diurnal variations were less marked.

The magnitude of the volatilization losses was in marked contrast to those obtained in studies of the volatilization rates of the same insecticides incorporated in the soil to a depth of 7.5 cm before planting a maize crop, where post-application losses over the whole growing season were 3% of the dieldrin and 7% of the heptachlor applied.

ACKNOWLEDGMENT

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Photodieldrin Formation and Volatilization from Grass

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Photodieldrin residues were detected on an orchard-grass pasture within 1 day after application of dieldrin at 5.6 kg/ha. Photodieldrin residues accumulated to a maximum concentration of 51 ppm (85 g/ha) 5 days after the application and then slowly declined to 9 ppm (30 g/ha) after 107 days. Dieldrin residues declined more rapidly and photodieldrin comprised one-third to one-half the total residues after the first 23 days. Vapor flux measurements showed that 2.75 g/ha of photodieldrin volatilized on the third day; this was 1% of the dieldrin volatilization on the same day. About 26 g/ha of photodieldrin was volatilized during the first 3 weeks after application. Later losses were very small. Photodieldrin residues were much less volatile than parent dieldrin.

Photodieldrin is a degradation product of the insecticide dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,-5,6,7,8,8a-octahydro-1,4-endo,exo-5,8-dimethano-naphthalene) that has been observed to form upon vegetation by photochemical reactions (Harrison et al., 1967; Ivie and Casida, 1971). Since there is evidence that photodieldrin is more toxic than dieldrin (FAO, 1971), the extent to which the conversion may occur under natural conditions and the mechanisms by which it may be distributed in the general environment are of considerable environmental interest. This paper presents quantitative results obtained on the amounts of photodieldrin formed from dieldrin residues on plant surfaces exposed to sunshine in the field. Estimates of the rate of volatilization of the photodieldrin residues relative to dieldrin are also presented.

EXPERIMENTAL SECTION

On July 12, 1973, dieldrin was applied as a spray of water-dispersed emulsifiable concentrate to a 2-ha area of an orchard-grass pasture at the Agricultural Research Center at Beltsville, Md., as described by Taylor et al. (1977). The nominal application rate was 5.6 kg/ha of active ingredient. No further treatments were applied, and the grass was not mowed after the application.

Sampling and Analysis. Soil and grass samples were taken from five sites within the treated area 3 h after application and at intervals up to 107 days (Taylor et al., 1977). Samples from each of the five sites were separately analyzed for both dieldrin and photodieldrin (Burke, 1969). The high concentrations of both compounds made clean-up unnecessary. All samples were quantitated by electron-

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capture gas chromatography. The compound appearing with the appropriate retention time for photodieldrin was isolated by Florisil PR column chromatography and its identity with photodieldrin II (1,9,10,10,11-exo-12-hexachloro-4,5-exo-epoxy-8,3,7,6-endo-8,9,7,11-exo-pentacyclo[7.3.0.0^{2,6}-0^{3,8}.0^{7,11}]dodecane) identified by Benson (1971) was confirmed by mass spectrometric comparison with Environmental Protection Agency reference material. No other degradation products were observed.

Dieldrin and photodieldrin in the air were adsorbed by passing air through 100-mL volumes of hexylene glycol contained in glass scrubbers mounted on masts at heights up to 100 cm above the grass (Taylor et al., 1977). Vapor density profiles of photodieldrin were measured in this way for consecutive 2-h sampling periods between 0400 and 2200 EDT on the third day after application. Dieldrin profiles were obtained for the same sampling periods. Dieldrin data were also obtained on the 1st, 2nd, 6th, 9th, 14th, and 23rd days after application. The hexylene glycol samples were protected from heat and light by coating the gas scrubbing bottles with aluminum spray paint and by storing the collected samples at 4 °C, in the dark, in bottles with tight fitting Teflon-lined caps. Such precautions reduced background contamination orginating from decomposition of the hexylene glycol. Caro et al. (1971) described the basic procedure for analyzing the hexylene glycol samples. Some samples contained low photodieldrin contents and required clean-up prior to EC–GLC analysis. Peroxide treatment with methanolic KOH (Glotfelty and Caro, 1970) was sufficient. The procedure gave quantitative recovery from fortified samples containing down to 10 ng of photodieldrin, using reflux periods of less than 30 min.

In addition to the multiple-height air samplers used to measure vapor profiles, a single hexylene glycol scrubber was positioned 20 cm above the ground in the center of the treated area on the 1st, 2nd, 3rd, 6th, 9th, and 23rd