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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-dimethanonaphthalene) 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-

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 originating 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

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Table I. Dieldrin and Photodieldrin Residues (mg/m² of Field Area) on Grass and Soil and Ratios of Photodieldrin/Dieldrin Residues in Grass and Air^a

Sampling time, days after application	Residues, mg/m ²					
	Dieldrin grass	Photodieldrin			Photodieldrin/dieldrin ratio	
		Grass	Soil	Total	Grass	Air
0.12	154 ± 25	1.5 ± 0.3	0	1.5	0.01 ± 0.001	0.008
2.0	99 ± 35	5.0 ± 0.8	0	5.0	0.07 ± 0.04	0.015
5.1	42 ± 9	8.5 ± 1.7	0	8.5	0.21 ± 0.01	0.016
8.0	29 ± 4	8.5 ± 1.5	0	8.5	0.30 ± 0.05	0.026
22	34 ± 3	11.2 ± 1.2	3.1	14.3	0.33 ± 0.03	0.016
35	14 ± 2	7.7 ± 0.2	2.5	10.2	0.61 ± 0.01	
55	12 ± 2	8.7 ± 0.8	4.0	12.7	0.74 ± 0.07	
79	7.7 ± 1.0	6.3 ± 0.7	5.4	11.7	0.87 ± 0.12	
107	5.9 ± 1.2	3.0 ± 0.6	7.2	10.2	0.61 ± 0.07	

^a All grass and soil residues are means of five samples; ± values are standard errors of means.

Table II. Photodieldrin (PhtDiel) and Dieldrin (Diel) Concentration in Air at Heights up to 1 m over Orchard-Grass Pasture 3 Days after Dieldrin Application at 5.6 kg/ha

Height, over grass, cm	Sampling period (EDT) and concn					
	0800-1000		1200-1400		2000-2200	
	PhtDiel ng/m ³	Diel μg/m ³	PhtDiel ng/m ³	Diel μg/m ³	PhtDiel ng/m ³	Diel μg/m ³
10	108	14.0	286	27.8	147	12.6
20	83.6	12.2	236	27.4	135	11.4
30	86.3	10.4	196	22.4	145	12.1
50	61.0	7.8	173	18.3	100	8.3
100	45.2	5.0	118	11.5	58.7	3.9
Mean PtD/Diel	0.0079 ± 0.0008		0.0095 ± 0.0008		0.0125 ± 0.0015	

days after the application. Air was drawn continuously through this scrubber at 0.5 m³/h for the entire period of air sampling (dawn to sunset) on these days, and the amounts of photodieldrin and dieldrin retained were measured.

RESULTS AND DISCUSSION

The results reported in Table I are the means of the pesticide contents found on the grass taken from the five sites. These data are presented as the amount of dieldrin present per unit area of ground surface (mg/m²). In the first few days after application, the dieldrin residues on the grass decreased rapidly, with only 27% remaining on the fifth day; the daily rate of loss decreased with time, with 9% remaining after 35 days. This loss could be accounted for by the measured volatilization (Taylor et al., 1977). Comparable results have been reported for dieldrin losses from vegetation by Harrison et al. (1967) and Dekker et al. (1970).

Although the photodieldrin content of the original formulation was negligible, the grass samples taken 3 h after application contained an average content of 8 ppm (1.5 mg/m²) of photodieldrin, corresponding to 1% of the dieldrin present. The weather was clear and sunny with little haze. The photodieldrin content rose to a maximum content of 51 ppm after 5 days, then decreased to 32 ppm after 35 days, and 9 ppm after 107 days. This decrease was partly due to the increase in dry matter created by growth. Calculation of the data in terms of mg/m² of field area (Table I) discounted this dilution. A similar pattern of photodieldrin accumulation was observed by Harrison et al. (1967) in southeastern England, who found that photodieldrin comprised 45% of the total residues present on the leaves of apple trees 11 weeks after dieldrin application, which is in almost exact agreement with the data of Table I.

Volatilization of Photodieldrin. Concentrations of photodieldrin (and dieldrin) measured in the air at five

heights during three sampling periods on day 3 are presented in Table II. The concentrations found between 1200 and 1400 EDT were the highest of the day for both compounds. Calculation of the photodieldrin/dieldrin ratios for each sampling revealed that, during a particular sampling period, the ratios were independent of height. The average values of the ratios, with standard deviations, are included in Table II. The constancy of these ratios with height confirms that the upward flux intensity of both compounds conforms to the equations

$$F_D \uparrow = K_z \quad (dc_D/dz)$$

$$F_{Pd} \uparrow = K_z \quad (dc_{Pd}/dz)$$

with identical values of the eddy diffusivity coefficient K_z . Relative flux intensities of the compounds may then be calculated by comparison of the slopes of the profiles (dc/dz) derived by plotting the concentrations as a function of height (Taylor et al., 1977).

Flux intensities of dieldrin and photodieldrin from the grass surface for each 2-h period on day 3 are presented in Figure 1. The curves are generally similar with a marked diurnal variation. The weather on this day was hot with clear sunshine, and the maximum evaporation was found at solar noon. Calculation of the ratio of the fluxes showed that the rate of photodieldrin volatilization relative to dieldrin increased steadily throughout the day, corresponding to the concentration ratios given in Table II. This change reflected the steady long period increase in the photodieldrin/dieldrin ratio on the grass shown by the data of Table I and showed no correlation with the diurnal variation of solar radiation. This indicates that the greater part of the photodieldrin in the air was evaporated from the grass rather than formed by photochemical degradation of the dieldrin vapor in the air. Integration of the curves of Figure 1 showed that over the whole day 282 g/ha of dieldrin and 2.75 g/ha of photodieldrin were volatilized from the grass.

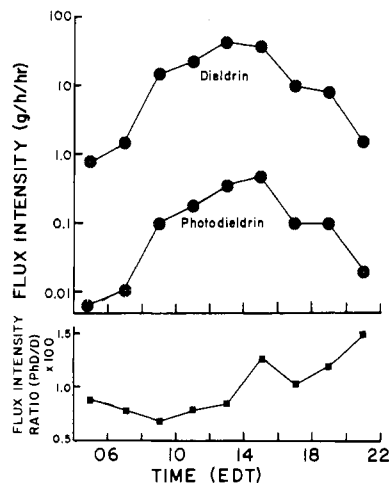


Figure 1. Vertical flux intensities of dieldrin and photodieldrin during 2-h sampling periods on the third day after application to orchard grass in July 1973; ratios are also included.

The ratios of photodieldrin/dieldrin residues found in the continuously run air samplers at the 20 cm height on the days of air sampling are presented in Table I. The value of 0.0015 obtained on day 3 (2 days lapsed time) was substantially in experimental agreement with the average value of 0.010 for the ratio of flux intensities and that of 0.0098 for the ratio of the amounts volatilized on that day. If it is assumed that the measured concentration ratios in the air reflect the relative amounts of photodieldrin and dieldrin volatilized on other days, they may be combined with dieldrin data presented by Taylor et al. (1977) to estimate the approximate total loss of photodieldrin to the air. This calculation indicates that a total of about 26 g/ha of photodieldrin were volatilized over the first 23 days, after which the rate fell to $0.1 \text{ g ha}^{-1} \text{ day}^{-1}$. The subsequent decrease in photodieldrin residues on the grass and soil was faster than this, indicating that chemical degradation was also taking place.

The ratio of the photodieldrin and dieldrin volatilization rates on day 3 does not represent a comparison of the specific volatilization rates per gram of residue because the

amount of photodieldrin present on the grass was only about 5% of the parent compound. Comparison of the calculated rates with the amounts on the grass indicates that, per unit weight of residue, the rate of photodieldrin volatilization was about one-fifth that of the dieldrin. Similar conclusions were reached by Harrison et al. (1967) and by Ivie and Casida (1971) in a study of photodieldrin formation upon bean leaves. Since the free evaporative conditions of the present experiment were far from equilibrium and the effect that the adsorption of the compounds on the leaf surfaces has upon their vapor pressures is unknown, no conclusions can be drawn from these observations concerning the relative equilibrium vapor pressure of the two compounds.

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