Volatilization of Dieldrin and Heptachlor from a Maize Field

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Dieldrin and heptachlor were applied at 5.6 kg/ha and mixed 7.5 cm deep in the soil immediately before maize planting on a 0.68-ha watershed at Coshocton, Ohio, on April 30, 1969. Vapor density profiles up to 4 m above the ground were measured on 7 days between May 2 and October 16. Vertical flux densities were calculated from eddy diffusion coefficients determined from simultaneous micrometeorological observations. Maximum flux intensities of 4.0 g/ha per day of dieldrin and 5.0 g/ha per day of heptachlor were observed on June 26th. Marked diurnal variations with noonday maxima were observed. Flux intensities declined to low values in October. Calculated seasonal losses were 199 g/ha of dieldrin and 383 g/ha of heptachlor.

The importance of volatilization as a significant pathway for organochlorine insecticide loss from soils was noted by Lichtenstein and Schultz (1961). Later, Lichtenstein et al. (1964) showed that losses of aldrin and dieldrin were greatly reduced when the insecticides were incorporated to the 4 in. depth in the soil than when they remained on the surface without cultivation; they attributed this difference to the higher evaporation of the exposed material. Toxic concentrations of insecticide vapors in the air over soils treated with aldrin, heptachlor, and other insecticides were demonstrated by Harris and Lichtenstein (1961) who also showed that the vapor concentration, measured in terms of toxicity, was affected by temperature, humidity, and airflow. Spencer et al. (1973) reviewed measurements of volatilization losses of various materials from several substrates including soil and plant surfaces, and discussed the mechanisms controlling the losses under field conditions.

Besides being a pathway of loss, vaporization can be a cause of contamination of plants, which can absorb the compounds directly from the air. Barrows et al. (1969) showed that the dieldrin distribution on maize plants grown on treated soil was consistent with accumulation by condensation rather than root adsorption and translocation. Similar distributions were reported by Caro (1971) for field-grown plants. Significant concentrations of dieldrin in the air over a treated field were revealed by exposing traps containing glass fiber filters at 30 to 60 cm heights above the soil. Over a 14-day period the traps accumulated up to 2.1 $\mu g/cm^2$ of filter area (Caro et al., 1971; Caro and Taylor, 1971). These results also indicated that the vapor concentrations decreased with time for 22 weeks after dieldrin incorporation at maize planting in early May.

The object of the present work was the direct measurement of the rate of volatilization of dieldrin and heptachlor from a field soil under conditions similar to those of normal agricultural practice. The techniques employed were those developed in other studies of the rates of gas exchange over soils and crop (Lemon, 1969). Vertical flux densities of dieldrin and heptachlor over

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treated soils were calculated from measured vapor concentration profiles and micrometeorological data. Observations were made on 7 days spaced over the growing season between maize planting and harvest.

EXPERIMENTAL SECTION

Experimental Site and Treatment. The experimental site was a small watershed (No. 109) at the North Appalachian Experimental Watershed at Coshocton, Ohio. This watershed is a 0.68 ha area of Rayne silt loam on a low hillside with an average eastward slope of 13.7%. The topsoil contains 2.2% organic matter, 15% clay, and 61% silt; the pH was 6.2. The watershed is a section of a larger field area of about 200 × 150 m with the longer axis oriented north and south. A weighing lysimeter of 16 m^2 field surface area is located within the field close to the northern outside edge of the watershed area. None of the soil in the whole area had previously received any dieldrin or heptachlor treatment.

The area was plowed, fertilized, and disked in early April 1969. On April 30, both dieldrin and heptachlor were applied together as a uniform spray of a single aqueous emulsion 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 dieldrin and heptachlor used were regular commercial formulations supplied by the Shell Chemical Company and Velsicol Corporation, respectively. Immediately after the application the soil was disked to a depth of 7.5 cm with a conventional two-gang disk with depth control wheels. Within 3 h of the treatment, the whole area including the lysimeter was planted to maize (*Zea mays*) in 107-cm rows oriented along the contours. The soil received no further cultivation until Oct 15, when the maize was harvested and the stover incorporated to a depth of 7.5 cm in two successive diskings with the same equipment.

Air sampling experiments were conducted on April 29, May 2, May 22, June 26, July 24, Aug 27, and Oct 14 and 16. The observations on Oct 16 were made over soil covered with plant debris after harvest and disking.

In additon to the air sampling experiments, the soil was sampled for insecticide analysis, immediately after cultivation on April 30 and again on Oct 17. The results of these analyses, with the details of the procedures, were reported by Taylor et al. (1971). On 4 air-sampling days maize plants were sampled for insecticide analyses; the procedure and results have been reported by Caro (1971).

Air Sampling. On each sampling date insecticide concentrations were measured at five heights up to 2 m above the ground or crop canopy at two locations on the

treated area, one in the center and one on the downwind edge. On July 24, Aug 27, and Oct 14 samples were also taken at five heights between the ground and the top of the crop canopy; on these days a full profile of vapor concentrations was obtained from the ground to 2 m above the canopy at the downwind edge of the treated area.

Pesticide samples were taken by drawing air through 100-ml volumes of hexylene glycol in glass scrubbers mounted on masts. The entry port to each scrubber was fitted with a widened tube containing a plug of glass wool to retain any particulate material. The exit of each was connected by rubber hose to a flowmeter leading into a surge tank exhausted by an electric vacuum pump. A single pump and surge tank drew air through the five scrubbers, and their individual flowmeters, mounted on each mast. Flow rates, controlled by screw clamps, were maintained at 7.8 l./min at all times. Data quoted elsewhere by Caro et al. (1971) and Parmele et al. (1972) should be corrected to this rate from the nominal value of 12.5 l./min. The vacuum pump was always placed on the ground several feet downwind from the sampling mast.

On the first 4 days, the scrubbers were run continuously for periods of 2 h, when each scrubber bottle was replaced with one containing fresh hexylene glycol. On and after Aug 27, 4-h sampling periods were used. The volumes of air drawn through each scrubber were therefore 936 and 1872 l., respectively.

Analytical Methods. The 100-ml volume of hexylene glycol was quantitatively transferred from each scrubber bottle to a 2-l. separatory funnel containing 1400 ml of 1% aqueous sodium chloride and 100 ml of n-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 layer was concentrated to 5–7 ml, using a Kuderna-Danish evaporative concentrator, and the concentrate was placed on a 10-g Florisil column. The heptachlor was eluted with 50 ml of 6:94 ethyl ether–hexane and the dieldrin was eluted with an additional 100 ml of 15:85 ethyl ether–hexane. The two eluates were received separately in Kuderna-Danish concentrators.

The heptachlor fraction was concentrated to 5–7 ml and subjected to further cleanup by chromatography on a column consisting of 0.7 g of activated charcoal and 2.2 g of Celite, eluting with 50 ml of 6:94 ethyl ether–hexane. The eluate was concentrated to 1 ml and a 3- to 8-μl aliquot was injected into a gas chromatograph equipped with a ^{63}Ni electron-capture detector.

The dieldrin fraction from the Florisil column was concentrated to 1 ml and a 3- to 8-μl aliquot was injected directly onto an alkaline precolumn within the gas chromatograph. The alkaline precolumn (Miller and Wells, 1969) effectively removed alkali-labile interferences and permitted unambiguous quantitation of dieldrin in the air extracts. It consisted of two 2.5-cm lengths of inert chromatographic support material, one carrying solid KOH and the other solid NaOH, placed in a series in the inlet end of the gas chromatograph column.

Suitable gas chromatographic conditions were: column, glass, 165 cm × 2 mm 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/m³, but it was necessary to analyze the extracts as soon after air sampling

Table I. Concentrations (ng/m³) of Dieldrin (D) and Heptachlor (H) at Various Heights over the Treated Area at Selected Times on May 22, June 26, and July 24

Date	Height (cm) above ground	Time period (EST) and insecticide concn			
		0400–0600		1400–1600	
		D	H	D	H
May 22, crop height 5 cm	10	51	203	214	534
	25	17	60	135	379
	50	11	18	102	187
	100	11	3	72	72
	200	12	3	62	36
		1000–1200		2000–2200	
		D	H	D	H
June 26, crop height 85 cm	100	249	187	84	118
	125	146	182	55	84
	175	109	131	47	65
	225	109	77	30	49
	275	87	81	28	43
		0400–0600		1200–1400	
		D	H	D	H
July 24, crop height 240 cm	25	183	282	271	601
	60	113	294	110	280
	120	89	144	76	104
	180	103	144	49	58
	240	60	69	45	22
	265	61	66	15	13
	315	53	64	16	17
	365	37	27	17	
	415	34	25	17	

as possible, because light-and heat-induced chemical reactions occurring within the hexylene glycol produce interferences that considerably reduced the sensitivity.

The pesticide content of the glass wool prefilters was determined by shaking the glass wool with n-hexane, concentrating the extract, and injecting an aliquot of the concentrate into the gas chromatograph.

RESULTS

Insecticide Concentrations in Air. Selected values illustrating the ranges of concentrations, or pesticide vapor densities, found on May 22, June 26, and July 24 are presented in Table I. The samples taken on April 29, before application of the insecticides to the soil, contained no measurable amounts of dieldrin or heptachlor. The data obtained on May 2 were very similar to those of May 22. With rare exceptions the vapor densities decreased with height above the ground or crop canopy. Vapor densities in the free air stream above the soil or crop tended to decrease over the growing season. The highest values found (not included among those presented in Table I) were 388 ng/m³ for dieldrin and 601 for heptachlor. These were observed close to the soil surface on July 24 under highly protected conditions below the mature crop and should not be compared with the values found in the free air stream above the canopy.

The vapor densities were lowest on Oct 14 when the standing crop was desiccated and withered after a period of dry weather. A marked increase was observed on Oct 16, after harvest and cultivation when the amounts of heptachlor found were comparable to those observed in May. The increase in dieldrin was less marked.

The amount of insecticides retained by the glass wool prefilters was always less than 3% of that retained by the hexylene glycol in the same period. Only dieldrin, and no heptachlor, was found on the glass wool. Little or no dust

was found on the prefilters; on almost all the observation days the soil surface was moist or consolidated with no dust blowing. Most dust collected appeared to be pollen. Although the filters may not have retained pesticide carried by fine aerosol particles, the possibility of significant transport of pesticide by soil dust may be discounted. If this occurred approximately equal amounts of dieldrin and heptachlor should have been found on the prefilters, whereas only dieldrin was detected.

Micrometeorological Observations. The pesticide vapor densities do not themselves indicate the rates of vertical pesticide movement out of the treated field. The vertical pesticide flux intensity, or flux density, $\uparrow P$, can, however, be related to the gradients of vapor density by eq 1, where $\partial p/\partial z$ is the rate of decrease of pesticide vapor

$$\uparrow P = K_z(\partial p/\partial z) \tag{1}$$

density (p), with height z, and K_z is the vertical eddy diffusivity coefficient at the particular height.

Since the value of the coefficient K_z depends upon the turbulent flow of the atmosphere into which the pesticide vapor is dissipated, it is a function of the meteorological conditions and not any physical or chemical property of the pesticide, provided that this behaves as a molecular vapor. The value of the coefficient may then be assumed to be the same as that for water vapor, defined by:

$$\uparrow E = K_z(\partial q_w/\partial z) \tag{2}$$

where E is the water vapor flux density and ($\partial q_w/\partial z$) is the water vapor concentration gradient. The value of the coefficient for solution of eq 1 or 2 must be determined from suitable meteorological data. The measurements taken during the present study together with a critical evaluation of their application have been described by Parmele et al. (1972) and will only be briefly reviewed here.

Instrumentation was available to determine the eddy diffusivity coefficient in three independent ways: (1) by direct observation of water fluxes using the lysimeter adjacent to the watershed; (2) by the Bowen ratio method for the calculation of the energy flux above the crop; and (3) by the aerodynamic method using profiles of wind speed with height.

In the first method water vapor fluxes, $\uparrow E$, were obtained directly from the weighing lysimeter located 15 m outside the north side of the treated area. This equipment, described by Harrold and Dreibelbis (1967), gives continuous records of weight changes in a 60 metric ton block of undisturbed soil to an accuracy of 2.25 kg. Water vapor profiles were measured above the crop with continuously recording wet and dry bulb thermometers mounted at appropriate heights above and below the crop canopy at the lysimeter and close to the pesticide sampling mast.

In the Bowen ratio method the value of K_z is given directly by the equation:

$$K_z = (R_n - G)/[q_a C_p(\partial t/\partial z) + \lambda(\partial q_w/\partial z)] \tag{3}$$

where R_n is measured net radiation, G is the soil heat flux, $\partial q_w/\partial z$ and $\partial t/\partial z$ are the humidity and temperature gradients, and λ is the psychrometic constant. q_a and q_w are the air and water vapor densities and C_p is the heat capacity of the air. The necessary observations of R_n and G were made at the lysimeter site. Surface soil temperatures were measured with an infrared thermometer.

In the aerodynamic approach the insecticide flux between two heights z_1 and z_2 is given by:

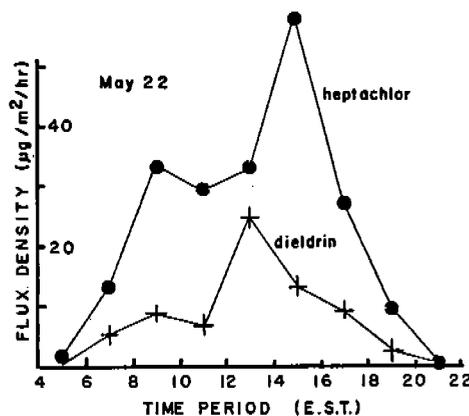$$\uparrow P = k^2(p_1 - p_2)(u_2 - u_1)/\Psi^2(\ln[(z_2 - D)/(z_1 - D)])^2 \tag{4}$$

Figure 1. Vertical flux densities ($\mu g/m^2$) of dieldrin and heptachlor during 2-h sampling periods on May 22.

where p_1, p_2, u_1, and u_2 are pesticide concentrations and windspeeds at the two heights. The parameter D is a crop displacement term and k is the von Karmen constant. The term Ψ is a correction factor which depends upon the thermal stability of the atmosphere; the choice of values used has been discussed by Parmele et al. (1972). The wind profiles necessary for calculations using eq 4 were measured with four rotating cup anemometers mounted at appropriate heights above the crop.

The appropriate values of the dieldrin and heptachlor profile gradients were obtained by plotting the observed vapor densities against the log height function in ($z - D$) and drawing a straight line through the points. The values of p_1 and p_2 for use in eq 1 and 4 were then read from the appropriate points on this line.

Pesticide Fluxes. Flux densities were calculated separately in three ways from the aerodynamic, Bowen ratio, and lysimeter observations. Good agreement was generally obtained between the Bowen ratio and lysimeter methods. The Bowen ratio was least reliable in the morning and evening hours, but the pesticide fluxes were then small. Aerodynamic data were suspect when the wind was light or the atmosphere was unstable and the necessary corrections were uncertain. The greatest confidence was placed in the flux rates obtained from the lysimeter data. Where these were unreliable for instrumental reasons or problems with wind fetch, Bowen ratio data were used. The pesticide profile data used were chosen from the two sites on the basis of wind speed and direction. The values from the mast at the downwind edge of the treated area were more consistent and reproducible than those at the center site.

Owing to sampling and analytical difficulties, limited information was obtained on May 2, but the data showed a decreasing dieldrin flux density from 22 $\mu g/m^2$ per h about noon to low values after 1800 EST. On this day the weather was warm and dry: surface soil temperatures reached 40 °C, the highest recorded in the whole experiment. Values of the Bowen ratio (the ratio of the energy used in heating the air to that used in evaporating water) ranged from 1.2 to 1.8, indicating that most of the radiant energy was converted in sensible rather than latent heat transfer.

Marked diurnal fluctuations in the flux densities were evident on May 22 and June 26 (Figures 1 and 2). May 22 was a cool overcast day with rain showers until about noon. Bowen ratios ranged from −0.4 to +0.4, indicating that most energy was used in latent heat flux. The data of June 26 are of particular interest. This was a clear warm day following a week of rain that had brought the soil to field capacity. Wind speeds ranged from 100 to 300 cm/s
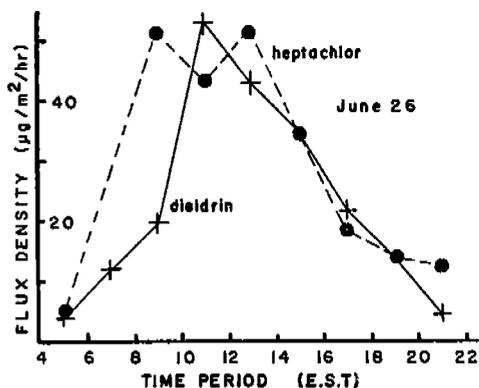
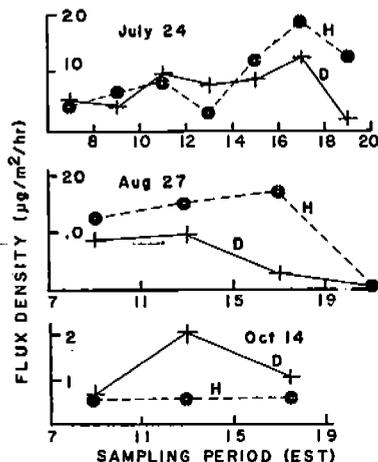**Figure 2.** Vertical flux densities ($\mu g/m^2$) of dieldrin and heptachlor during 2-h sampling periods on June 26.

Figure 3. Vertical flux densities ($\mu g/m^2$) of dieldrin and heptachlor during 2- or 4-h sampling periods on July 24, Aug 27, and Oct 14.

(2–6.5 mph). The meteorological data showed that almost all the energy was used in evapotranspiration and the moisture loss from the lysimeter was one of the highest recorded on a single day at the Coshocton station. Conditions were therefore very favorable for pesticide volatilization and the rates presented in Figure 2 may be close to the highest that can be expected from organochlorine insecticides incorporated into field soils under Ohio conditions. Maximum surface soil temperatures on May 22 and June 26 were 20 and 31 °C, respectively.

Although diurnal variations were evident on July 24, Aug 27, and Oct 14, the flux densities showed a general decline (Figure 3). On July 24 the soil was still moist and the crop canopy was fully closed at a height of 240 cm. On Aug 27 only about $2/3$ of the radiant energy was converted to latent heat flux. The maximum surface soil temperature was 28 °C on both July 24 and Aug 27. On Oct 14 the crop was dry, withered, and ready for harvest. The day was overcast with light and variable winds. Radiant energy was about equally distributed between sensible and latent heat transfer.

The data of Oct 16 showed very large increases over Oct 14 in concentrations and flux of heptachlor and smaller increases for dieldrin. The marked increases were clearly due to the cultivation which brought fresh damp soil to the surface. Flux densities of both compounds declined rapidly throughout the day, dieldrin falling from 14 $\mu g/m^2$ per h in the morning to 2.0 in the evening, and heptachlor from 84 to 34. This rapid decline, which was parallel to the concentrations in the air, suggested that the increase was of short duration.

Table II. Daily Flux Densities of Dieldrin and Heptachlor (Grams/Hectare) from Treated Area on 7 Sampling Days between May 2 and Oct 16, 1969

Date	Daily flux density, g/ha	
	Dieldrin	Heptachlor
May 2	0.89	0.59
May 22	1.41	4.10
June 26	4.00	5.00
July 24	1.03	1.31
Aug 27	0.87	1.80
Oct 14	0.15	0.07
Oct 16	0.9	8.0

Table III. Concentrations (ng/m^3) of Dieldrin and Heptachlor at 100 and 225 cm Heights on June 26

Height above ground, cm	Time period, EST				
	0400–0600	0800–1000	1000–1200	1600–1800	2000–2200
	Dieldrin				
100	55	129	249	72	84
225	21	75	109	40	30
	Heptachlor				
100	112	195	187	334	118
225	17	66	77	160	49

The total daily fluxes of both pesticides presented in Table II were calculated by integration of the curves in Figures 1, 2, and 3. The data for May 2 were estimated by extrapolation to zero fluxes at 0900 and 1900 EST.

Soil Analyses and Soil Conditions. Samples of soil were taken to a depth of 23 cm on May 1, within 24 h of application and at intervals of 6 months or a year until 1973. The results, which have been reported by Freeman et al. (1975), show that about 4.5% of the dieldrin and 12.5% of the heptachlor disappeared from the soil between May 1 and Oct 17. These results indicate that the decrease in volatilization over the period of observation was not due to an exhaustion of the amounts of residues present in the soil as a whole.

Pesticide Degradation Products. No measurable quantities of any degradation or conversion product of either insecticide were found in the air. On Oct 17, heptachlor epoxide was found in the soil in an amount equivalent to 15% of the original heptachlor (Freeman et al., 1975). Plant tissue analyses reported by Caro (1971) revealed increasing amounts of dieldrin, heptachlor, and heptachlor epoxide on the maize leaves over the growing season. The residues of the parent compounds were accumulated directly from the air, while the epoxide was formed in place from the accumulating heptachlor. No photodieldrin was found in the air or plants at any time.

DISCUSSION

Soil and Crop Conditions Affecting Volatilization Rates. The most striking features of the data are the marked diurnal variations in flux densities of both insecticides observed during the period of most intense volatilization on May 22 and June 26, and the long-period decrease to lower values in August and September. Detailed examination of these changes permits some inferences to be made on the relative importance of the factors that control the rate of volatilization loss.

The diurnal variations are shown by both the flux densities and the vapor concentrations of both insecticides: the changes in vapor concentration (vapor density) are illustrated by the data of Table I. More complete results for both insecticide concentrations at two selected heights throughout the day on June 26 are presented in Table III. Comparison of either flux or vapor densities with soil temperature revealed no significant relationship on either

a diurnal or a seasonal basis.

The vapor densities observed were always a small fraction of the saturation equilibrium values of both compounds. The highest dieldrin vapor density observed was 388 ng/m³, 25 cm above the soil on July 24 when the soil temperature was 21 °C. The saturation vapor density of pure dieldrin at 21 °C is 65 ng/l. (Spencer and Cliath, 1969); the relative vapor density was therefore 0.6%. This was the highest value observed in the entire experiment. The vapor density in equilibrium with dieldrin absorbed on soil is, however, much lower than that of the pure compound and varies with the amount in the soil. The dieldrin concentrations in the top 7.5-cm layer of field soil were between 2 and 4 ppm. Spencer et al. (1969) showed that the vapor density of dieldrin in air passing over Gila silt loam containing these amounts ranged from 3 ng/l. at 20 °C to 15 ng/l. at 40 °C. This indicates the value of 388 ng/m³ represents about 11% of the vapor density at equilibrium between the atmosphere and the adsorbed dieldrin. The vapor densities in the air 25 cm above the field surface were therefore highly unsaturated with respect to the soil dieldrin. If the upward flux of the pesticides was controlled by the turbulent diffusion through the air, considerable accumulations would be expected under quiet conditions in the morning and evening with vapor densities approaching those in equilibrium with the soil. No such accumulations were observed, and on May 22 and June 26 maximum concentrations close to the ground were observed at midday, when fluxes were greatest. Atmospheric diffusion was therefore never rate limiting and the flux density was controlled by the rate of vaporization from the soil surface. This conclusion was confirmed by calculation of the "residence time" of the insecticides within a 1 m depth of air above the soil or crop canopy. "Residence time" was defined as the amount present in this 1 m layer divided by the flux density through it. This time was generally between 10 and 20 s except in the early morning hours when it increased to between 3 and 5 min. The shortness of these times indicated a rapid dispersal of the insecticides after they had left the soil surface.

The relative importance of diffusion and mass flow of soil water in maintaining pesticide concentrations at the surface of the soil has been discussed by Spencer et al. (1973). Data from laboratory experiments with dieldrin in Gila silt loam described by Spencer and Cliath (1973) showed that during an initial period of about 25 days the volatilization rate fell steadily as the surface was depleted and upward movement became dependent upon diffusion of dieldrin from the lower layers. When the relative humidity of the air over the soil was reduced below 100% and upward movement of soil water began, the volatilization rate increased as the surface layer was replenished by dieldrin carried upward by mass flow. Calculations of the amounts of dieldrin brought to the surface by mass flow, based upon estimates of dieldrin concentrations in the soil solution, were in excellent agreement with the observed values. On a daily basis these values ranged between 6 and 10 μg/m² per h depending upon the amount of water loss. In view of the differences between soils and experimental conditions the agreement between these results and those presented in Figures 1 and 2 must be considered excellent. In the experiments of Spencer and Cliath the dieldrin was thoroughly mixed throughout a specially prepared laboratory sample of soil, and the initial decrease in diffusion rate was shown to correspond to surface depletion. In our field experiments the mixing was much less efficient and diffusion of the dieldrin and heptachlor was probably inhibited by the absorption of the

insecticides on "untreated" soil brought to the surface during the cultivation. The basic diffusion component of movement would then be less important so that the importance of mass flow was enhanced. The diurnal variations in flux densities may therefore be attributed to changes in upward movement of soil moisture in response to the diurnal variation of water evaporation at the soil surface. Jackson et al. (1973) have demonstrated that the upward movement of water through the top 3 cm of soil responds directly to solar radiation with a marked maximum in the early afternoon hours.

Further confirmation of this mechanism, described by Hartley (1969) as the "wick effect", is provided by the correlations between 2-h water loss and insecticide flux densities on May 22. On this day the young maize plants were 5 cm high, and water loss by transpiration may be neglected. Statistical analysis showed that the dieldrin flux was related to water loss with a correlation coefficient of 0.47, and the heptachlor coefficient was 0.93. The poorer coefficient for dieldrin was due to the high flux between 1200 and 1400 EST which preceded the maximum heptachlor flux and water evaporation between 1400 and 1600 EST; it is probable that better correlations would have been obtained if pesticide data had been available over shorter sampling times.

The data of July 24, Aug 27, and Oct 14 are more difficult to interpret. The lower flux densities may be in part due to the reduction in moisture loss from the soil surface due to shading of the surface by the crop canopy, which closed in early July. Increased transpiration of water by the plants, which should be distinguished as a separate pathway of water loss from evaporation at the surface, reduced the moisture content of the whole profile. This, together with the higher relative humidity under the canopy, decreased upward movement to the surface.

The large differences in flux densities between Oct 14 and 16, following cultivation on Oct 15, were considered to be due to the exposure of fresh moist soil in which the pesticides had been sealed by drier layers above. The soil was moistened by a light early morning rain which would strongly enhance the release of adsorbed insecticide as observed by Spencer and Cliath (1973). October 16 was a cool and cloudy day and the energy balance was dominated by advection from a fresh northwest wind, suppressing conditions which would lead to marked diurnal variations in flux densities.

Total Seasonal Loss. The total seasonal loss may be estimated by integrating the curves obtained by linear interpolation of the data in Table II. Excluding the Oct 16 losses, these estimates are 244 g/ha of dieldrin and 390 g/ha of heptachlor.

A more refined estimate can be made if it is assumed that the loss is mainly controlled by the energy budget at the soil surface, as implied by the wick effect hypothesis. Daily water losses from the surface are not known, but the daily records from weighing lysimeter provided a measure of total evapotranspiration. The ratio of dieldrin loss to evapotranspiration was calculated for each observation day except Oct 16: the units of this ratio were grams/(hectare inch), or (ppb) × 4.0 as a solution concentration. The resulting points, plotted in Figure 4A, were smoothed to a curve giving an estimate of the ratio over the growing season. During May and early June, where the slope of this curve is low, most of the water loss was due to evaporation from the soil. The rapid decrease in the ratio after late June coincides with the close of the crop canopy, when surface shading became almost complete and water loss by transpiration through the plants became dominant.
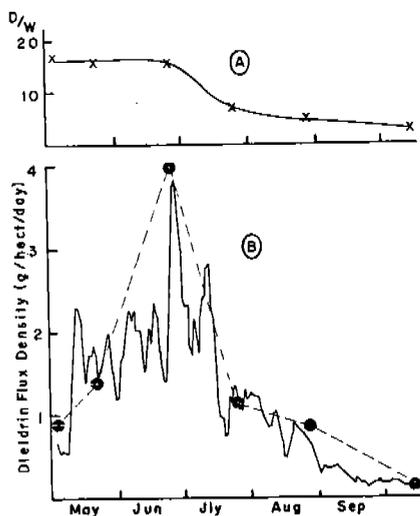
Figure 4. (A) Ratio of dieldrin/water loss (grams/(hectare inch)) from May 4 to Oct 14. (B) Five-day running means of estimated daily dieldrin volatilization from May 3 to Oct 14, with measured dieldrin volatilization on May 2 and 22, June 26, July 24, Aug 27, and Oct 14.
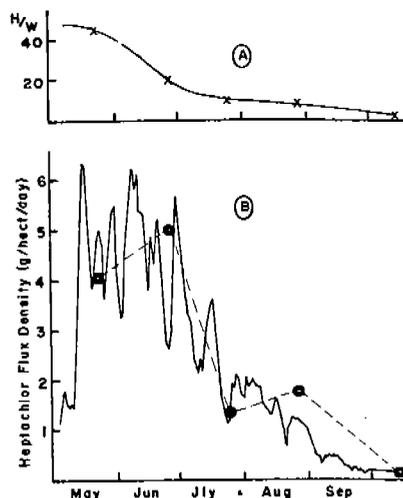

Figure 5. (A) Ratio of heptachlor/water loss (grams/(hectare inch)) from May 4 to Oct 14. (B) Five-day running means of estimated daily heptachlor volatilization from May 2 to Oct 14, with measured heptachlor volatilization on May 22, June 26, July 24, Aug 27, and Oct 14.

Values of the dieldrin/water loss ratio taken from this curve were then used, with the daily lysimeter data, to calculate the daily dieldrin volatilization. Summation of the results from May 3 through Oct 14 gave a revised estimate of 199 g/ha for the seasonal loss of dieldrin. This is equivalent to 3.6% of that applied in the original spray. It does not include any losses by drift or evaporation during the spray operation.

The estimated daily losses showed wide variation ranging from 4.6 g/ha on June 27 to 0 on July 5; the latter was a cloudy day of heavy rainfall. For convenience, the data are presented in Figure 4B in terms of 5-day running means. This figure also contains the individual daily observations with the linear interpolation. The difference between the two estimates of the seasonal loss is clearly due to the overestimate by linear interpolation between May 25 and June 26. As noted above the latter was a day of high evaporation and dieldrin volatilization. The linear interpolation also gave overestimates in August and September.

Comparable data for heptachlor are presented in Figures 5A and 5B. The corrected estimate for seasonal loss of heptachlor was 383 g/ha, or 6.8% of the application. The range of heptachlor/water loss ratios was greater than for dieldrin due to higher volatilization of heptachlor in May and June. The onset of the decrease in the ratio preceded that of the dieldrin by about 20 days, but the curves were nearly parallel after early July. The reason for the difference is not known, but the higher heptachlor volatilization may have caused a more rapid depletion in the amount present in the soil pores in the surface layer. The highest estimated daily heptachlor volatilization was 10.1 g/ha on May 27.

Volatilization in the Second Year. After plowing and discing in the spring of 1970, the area treated in 1969 was resown to corn. No fresh insecticide was applied. On Aug 26, 1970, air samples were taken at heights from the ground up to 430 cm. The mature crop was 230 cm high. Samples taken between 1000 and 1600 EST at heights between 50 and 200 cm above the canopy contained dieldrin concentrations between 0.6 and 0.3 ng/m³, and heptachlor concentrations from 0.5 to 0.3 ng/m³. Since no meteorological observations were made, flux densities cannot be calculated directly, but estimates can be made by assuming that the K_z were similar to those in 1969. Since the

dieldrin vapor densities were only 5–8% of those in 1969, and the heptachlor about 3%, it may be concluded that the volatilization losses in the second year were less than 10% of those in the first. This implies that less than 2 g/ha of dieldrin and 40 g/ha of heptachlor were volatilized in the second year. No data are available for subsequent years.

Adsorption of Insecticides by Corn Leaves. Data on the amounts of dieldrin and heptachlor accumulated by the corn leaves have been presented by Caro (1971). The accumulation took place slowly over the growing season to reach maximum values of 1.33 ppm of dieldrin and 0.14 ppm of heptachlor on the lower leaves. The total residue was a small fraction of the amount that had volatilized through the crop. As noted by Caro (1971) this accumulation is a very inefficient process. Measurements of the adsorption of dieldrin by corn leaves from air containing known concentrations of dieldrin made in the growth chamber (B. C. Turner, unpublished data) have demonstrated that the adsorption is highly sensitive to the relative humidity of the ambient air. Dieldrin adsorbed by dry leaves was very rapidly desorbed under the moist conditions that are frequent at night in the field. It is likely that the accumulation rate is dependent upon the rate of diffusion of the adsorbed insecticide into the interior of the plant leaves, where the re-evaporation of the residues is less sensitive to micrometeorological changes and the condition of the leaf surface.

On examination of the upward flux densities at various levels under the crop canopy, Parmele et al. (1972) indicated no measurable adsorption by the leaves. Calculation of flux densities within the canopy presents considerable difficulties because of the special distribution of sources and sinks within the "roughness" elements themselves.

Losses during Application. No measurements were made of insecticide concentrations in the air over or downwind of the field during the application. The amount lost during the application can, however, be estimated from the soil analyses reported by Freeman et al. (1975). The mean concentration of both compounds in the five samples taken on May 1 was close to 1.45 ppm; standard errors of the means were 0.19 ppm. Since all the samples were taken to a depth of 23 cm with a corer of known diameter and the total weight of each was measured, the concentration

was found equivalent to 320 mg/m² of the field surface with a standard error of ±42 mg/m². This indicates that 2.4 kg/ha or 43% of the initial application was not accounted for, with a 95% confidence that the actual loss was between 29 and 57%.

Analysis of soil surrounding another field sprayed in the same way in 1968 (Caro, 1971) showed limited local deposition of drift, suggesting that almost all the lost material was injected into the atmosphere by evaporation of spray particles or from the treated surface before incorporation. It is thus clear that the amounts of soil-incorporated dieldrin and heptachlor volatilized to the air over the growing season were between 10 and 25% of those entering the atmosphere during the application.

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Supplementary Material Available: A detailed map of the experimental field (Figure A) and tabulations of insecticide concentration as a function of height for each observation day (Tables A–E); 6 pages. Ordering information is given on any current masthead page.

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Determination of Malathion, Malaoxon, and Mono- and Dicarboxylic Acids of Malathion in Fish, Oyster, and Shrimp Tissue

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A method is described for monitoring the presence of malathion and its metabolites in the aquatic environment. Malathion, malaoxon, malathion monoacid, and malathion diacid were determined in fish, oyster, and shrimp tissues by gas–liquid chromatography (GLC) using phenthoate and phenthoate acid as internal standards. GLC analyses were performed without cleanup, using a flame photometric detector operating in the phosphorus mode. Acid compounds were methylated with diazomethane. Pinfish exposed to 75 µg/l. of malathion in flowing seawater for 24 h contained no residues of malathion or malaoxon, although the concentration of the malathion monoacid in the gut was 31.4 µg/g. The data illustrate that pinfish rapidly convert malathion to the mono- and dicarboxylic acids of malathion.

Malathion (O,O-dimethyl dithiophosphate of diethyl mercaptosuccinate) has a broad spectrum of effectiveness against insects and is widely used along coastal areas for control of mosquitoes, flies, and other noxious pests. Although the chemistry and metabolism of malathion in various substrates have been studied extensively (Krueger and O'Brien, 1959; Corley and Beroza, 1968; Shafik and Enos, 1969; Shafik et al., 1971; El-Refai and Hopkins, 1972; Wolf et al., 1975) practically no residue data have been reported for malathion or its degradation products in aquatic species.

Binder (1969) studied the uptake of malathion in carp exposed to 5 mg/l. malathion for 4 days and found that residues in the flesh had an average half-life of 12 h, the liver concentrating the greatest amount. At our laboratory,

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