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Volatilization of Dieldrin from Fallow Soil as Affected by Different Soil Water Regimes[1]

G. H. Willis, J. F. Parr, S. Smith, and B. R. Carroll[2]

ABSTRACT

Dieldrin was surface applied at a rate of 782 g/plot to 3 15.2- by 22.9-m plots [10 ppm based on a 2 X 10^6 lb soil/acre 15.2 cm (6 inches)]. Immediately after application, 1 of 3 soil water regimes (flooded, moist, nonflooded) was imposed on each plot. An air sampling system was used to measure the atmospheric concentration gradient of dieldrin between 10 and 30 cm above each plot. Calculations based on the aerodynamic method indicated that approximately 18% of the applied dieldrin volatilized from the moist plot in 5 months, whereas only 2 and 7% volatilized from the flooded and nonflooded plots, respectively. Multiple regression analysis indicated that of the climatic variables measured, temperature had the greatest effect on dieldrin volatilization. There was no apparent dieldrin degradation in any of the plots.

Additional Index Words: turbulent transfer, dieldrin degradation

The ultimate fate of certain chlorinated hydrocarbon pesticides in the environment has been the subject of considerable research effort in recent years. Compounds such as dieldrin tend to accumulate in soil because of their relative *resistence* to degradation through either chemical or microbiological processes. A number of mechanisms of adsorption and desorption of these compounds with soil organic and inorganic components has been demonstrated. Moreover, the rate and the extent of degradation of some pesticides by soil microorganisms under specific environmental conditions, losses through runoff and leaching, as well as absorption by plant roots, have been reported. Nevertheless, many researchers continue to report that large amounts of these chemicals remain unaccounted for even in carefully controlled field experiments. Volatilization losses of these pesticides directly to the atmosphere from the site of application is considered to be a distinct possibility.

A number of reports indicate that although many pesticides have relatively low vapor pressures, extensive volatilization can occur under certain laboratory and field conditions (Bramesberger and Adams, 1966; Gray, 1965; Harris and Lichtenstein, 1961; Hinden, May, and Dunstan, 1966; Starr and Johnsen, 1968; Willis et al., 1969; Willis, Parr, and Smith, 1971). However, information on the volatilization potential of field-applied dieldrin is quite limited.

In laboratory studies using a gas-saturation technique, Spencer and Cliath (1969) and Spencer, Cliath, and Farmer (1969) found the vapor density of solid-phase dieldrin, and dieldrin mixed with soil, to be 3 to 12 times greater than predicted from published vapor pressure values. They also reported that dieldrin vapor density increased with temperature and concentration, but that vapor density was not affected by soil-water content until the water content decreased below the equivalent of 1 molecular layer of water, whereupon vapor density dropped to very low values. Thus, from their data one can conclude that loss of water, i.e., codistillation, was not required to attain maximum dieldrin vapor density. Wheeler (1969) and Acree, Beroza, and Bowman (1963) reported volatile losses of dieldrin and DDT from aqueous solutions by codistillation. Barrows et al. (1969) attributed the higher concentration of dieldrin in field-grown corn leaves (*Zea mays* L.), compared with protected greenhouse-grown corn leaves, to aerial contamination resulting from volatilization of dieldrein applied to the soil surface.

Earlier reports by Willis et al. (1969, 1971) describe a system for measuring atmospheric concentration gradients of field-applied pesticides. The use of these data with the aerodynamic method for estimating flux should provide a means for characterizing pesticide volatilization losses under field conditions. The aerodynamic method provides a positive measurement technique and should be more acceptable than indirect methods that depend upon measuring differences between the amount applied and that recovered from the soil, plant, and runoff in either the original or degraded forms. More detailed discussions of turbulent transfer and the use of the aerodynamic approach to measure flux are available (Deacon, 1949; Priestly, 1959; and Webb, 1965).

The objectives of this paper were to evaluate the extent of dieldrin volatilization from fallow soil, using an aerodynamic method for estimating flux, and to investigate effect of different soil water regimes on dieldrin volatilization.

THEORETICAL CONSIDERATIONS

The aerodynamic method was used to estimate pesticide volatilization or flux, which in this case is the amount of pesticide transported vertically (turbulent transfer) from a unit area of soil surface per unit of time and is defined as

$$\text{Flux} = K_p \, dc/dz \qquad [1]$$

where K_p is the transfer (diffusivity) coefficient for the pesticide and dc/dz is the pesticide atmospheric concentration gradient. The transfer coefficient is defined by

$$K_p = k\,(z + z_o)\,U_* \qquad [2]$$

where k is the von Karman constant (0.4), z is the measurement height (cm), z_o is the roughness length (cm), and U_* is the friction velocity. The roughness length is the distance above the soil surface at which wind velocity becomes 0 because of frictional drag due to surface roughness. The friction velocity is a representation of shearing stress or loss of momentum from the horizontal drag of wind on the ground surface and is defined as

$$U_* = U_z\, k/\ln\,[(z + z_o)/z_o] \qquad [3]$$

where U_z is the wind velocity at the measurement height and k, z and z_o are defined as before. Equation [3] is the log wind profile

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[2] Soil Scientist, Microbiologist, Chemist, and Soil Scientist, respectively, USDA-ARS-SWC, Baton Rouge, La.

equation solved for U_* rather than U_z. Equations [1], [2], and [3] are best applied with data time-averaged over periods of 15 min to 1 hour.

One of the factors that must be given careful consideration in this type of study is the fetch/height ratio. Fetch is the distance between the edge of the plot and the site within the plot where aerodynamic parameters are measured and atmospheric samples are taken, and height is the sampling height. When air, passing over a surface of given roughness, wetness, and temperature, moves over a second (different) surface, its velocity, temperature, and vapor profile changes from that determined by properties of the first surface to one resulting from properties of the second. The new equilibrium profile is not established immediately throughout the layer that is measured. Thus, the fetch must be large enough to permit sampling far enough from the plot border to ensure the establishment of a new equilibrium at a specific sampling height. Agreement on the minimum acceptable fetch/height ratio is somewhat lacking since it is so dependent on windspeed during the sampling period. Generally, however, it is believed that ratios should not be less than 50 to 100.

MATERIALS AND METHODS

Formulations of dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4:5,8-dimethanonaphthalene) have been either soil incorporated or surface applied, depending on specific conditions and objectives. However, in the present study to enhance the volatilization potential, dieldrin was surface-applied to three 15.2- by 22.9-m fallow plots of Commerce silty clay loam (an alluvial soil with 0.83% organic matter and pH 6.2) at a rate of 782 g/plot, or equivalent to approximately 10 ppm, assuming a uniform soil density of 2 by 10^6 lb/acre and uniform mixing to a depth of 15.2 cm (6 inches). The plot area was on relatively flat land free of obstructions that might cause undue turbulence, and grass borders were kept closely mowed. Immeidately after dieldrin application, one of three soil moisture regimes was imposed on each plot for the duration of the experiment: (i) flooding to a depth of 10 cm; (ii) moist; and (iii) nonflooded, in which no water was applied other than natural rainfall. Dieldrin volatilization with time was then monitored continuously with a special air sampling apparatus designed for that purpose. The moist plot was maintained by sprinkling 2 to 3 times daily to maintain soil moisture in the 1/3- to 1-bar range. The flooded plot was excavated to a depth of 12 cm and the water level was maintained at a depth of 10 cm.

Space limitations imposed in meeting the necessary fetch-height ratio restricted the number of plots to three. Since replication of the soil water regimes was not feasible, strict interpretation of the results presented here is somewhat limited. Nevertheless, this information should be useful in characterizing relative differences among various soil water regimes on dieldrin volatilization.

The air sampling system for monitoring atmospheric concentration of dieldrin was essentially the same as that reported earlier (Willis et al., 1969, 1971). Sampling booms were positioned horizontally, 10 and 30 cm above either the soil or water surface, with each connected to a pesticide vapor trap consisting of a 1,000-ml Erlenmeyer flask containing 500 ml of ethylene glycol previously washed with benzene to remove impurities that might interfere with gas chromatographic analysis of dieldrin. Air at each elevation above the plot was drawn with a vacuum pump through the booms and into the traps that were fitted with gas dispersion tubes to ensure maximum trapping efficiency. A flow rate of 1 liter/min, measured with a rotometer-type flowmeter, was controlled with a needle valve installed between the boom and the trap.

Windspeed and direction at 20 cm above the plot surface were measured continuously with a Belfort wind direction transmitter (5-363D) and two totalizing anemometers (5-349) used with a strip chart recorder. Air temperature at 10 and 30 cm was monitored with thermocouples and a temperature recorder. Pan evaporation and precipitation also were recorded throughout the study.

At intervals ranging from 4 hours at the start of the experiment to 21 days later on, the pesticide traps were replaced and removed for analysis. Dieldrin was extracted from the ethylene glyco benzene (250 ml), using a magnetic stirrer for 1 hour. Th solvents were partitioned in a separatory funnel and the et glycol was discarded. The benzene was washed 3 times with dried with anhydrous Na_2SO_4, and concentrated to an appro volume for gas chromatographic analysis. Previous studi standard dieldrin solutions showed that this extraction an centration procedure could account for 90±1% of the t dieldrin. No adjustments were made in subsequent calculati the 90% recovery factor.

The degradation of soil-incorporated dieldrin as affected 3 water regimes was evaluated on three separate 1.5- by 1.5 low plots adjacent to the volatilization plots. Soil was exca from each plot to a depth of 15 cm, screened through a 6. (1/4 inch) hardware cloth, and weighed. Based on the ove moisture content of soil, a predetermined amount of dieldr mixed with the soil from each plot to achieve an intende centration of 10 ppm. To ensure complete homogeneity, so pesticide were mixed for 30 min in a cement mixer. The so then returned to the plots and the water treatments were imp

At monthly intervals soil samples were taken from each small plots and were analyzed for dieldrin degradation. Th cedure followed for extraction and analysis of dieldrin was to that reported earlier for soil-applied DDT (Parr et al., 1 About 20 g of soil (oven-dry weight basis) was extracted w 1:1 benzene-methanol solution. After brief manual stirr mixture was allowed to stand overnight prior to sonification a Branson Model J-17A Sonifier, which ensured thorough and homogenization of soil and extractant. Sonification reduced soil extraction time, compared to previously used, methods (Willis et al., 1971). Samples were subjected to th min sonification periods, each followed by decantation o supernatant solution and addition of fresh aliquots of extr solution (125 ml). The decanted volumes were combined separatory funnel, washed 3 times with distilled water, dried anhydrous Na_2SO_4, and concentrated for gas chromatog analysis.

Aliquots (5 µliter/injection) of the benzene extracts fro and soil samples were assayed for dieldrin with a Micro-Tek 220 gas chromatograph equipped with a ^{63}Ni electron captu tector and an Infotronics Digital Integrator Model C Operating parameters were:

Column: Glass, 180 cm × 6 mm, packed with mesh Chromsorb W High Performanc DMCS coated with 3% OV-1.

Temperatures:	Oven	190C
	Detector	260C
	Inlet	200C

Carrier Gas: N_2 (prepurified) at 115 cc/min.

High purity dieldrin for use as an analytical standard w plied by the Shell Chemical Co.

(*Mention of trade names or commercial materials is for c* venience of the reader and does not constitute any pre endorsement by the US Department of Agriculture, ove products available.)

RESULTS AND DISCUSSION

The degradation phase of this investigation that little or none of the soil-incorporated diel degraded after 6 months under any of the thre regimes. Samples taken throughout the study, a depths from 0 to 15 cm, showed that a very unifo tribution of dieldrin resulted from mixing the s soil and pesticide in a cement mixer. Concen based on the oven-dry weight of soil, ranged fro 14 ppm, somewhat higher than the intended con tion of 10 ppm.

Changes in the mean atmospheric concentra dieldrin, 10 and 30 cm above the soil or water su subjected to different water regimes, are shown in Table 1. Maximum concentrations for all treatments at each sampling heights were attained the 1st sampling day, except above the moist plot at 10 cm where the highest values were measured during the sampling periods beginning Sept. 14, Sept. 19, and Oct. 3. After about 4 weeks, dieldrin concentrations above all plots tended to decrease and were low for the remainder of the study.

In some cases, the atmospheric dieldrin concentrations during the 1st two sampling periods were greater 30 cm above the plot surfaces than at 10 cm. These negative concentration gradients are thought to have resulted from the formation of an air temperature minimum at a height greater than 10 cm during nighttime temperature inversions.

A secondary air temperature minimum above the soil surface would result in a layer of relatively dense air, within which pesticides could accumulate, causing higher atmospheric concentrations within the zone of minimum temperature, compared with air above or below this zone. Geiger (1965) suggested that this particular phenomenon occurs frequently, especially in warmer climates. Air temperature measurements at 10 and 30 cm above the plots during the first 24 hours indicated that temperature inversions occurred over the moist and nonflooded plots, beginning near sunset and continuing until dawn. Moreover, on several occasions the nighttime temperature at 30 cm was lower than at 10 cm, indicating the presence of a colder air layer or secondary minimum above the plots. Air temperature was not measured at heights greater than 30 cm, thus, it is uncertain whether a true air temperature minimum existed above 10 cm or whether the temperature profiles were oscillating between inversion and noninversion. During these inversions little or no air movement occurred between 2300 and 0700 hours. Temperature inversions were not detected over the flooded plot during the first 24 hours.

A summary of the climatological data monitored throughout the study is shown in Table 2. September and October were relatively warm and dry, with high evaporation rates and little wind; November was a transition month; December and January were cold and wet, with low evaporation and higher winds.

Table 1—Atmospheric concentration of dieldrin 10 and 30 cm above the water or soil surface of plots subjected to different water regimes

[illegible] of [illegible] period	Atmospheric concentration, μg/m³					
	Flooded		Moist		Nonflooded	
	10 cm	30 cm	10 cm	30 cm	10 cm	30 cm
[illegible]	14.5	12.2	9.8	12.4	7.9	8.2
[illegible]-10	4.1	5.5	5.4	2.8	3.0	4.4
[illegible] 11-13	0.9	0.8	6.1	1.8	0.5	0.4
[illegible] 14-18	3.6	3.5	16.2	9.9	3.9	2.7
[illegible] 19-24	3.3	2.8	26.9	7.1	4.9	2.9
[illegible] 25 - Oct. 2	1.1	0.8	7.5	2.2	1.1	0.3
[illegible] 3-9	3.2	2.0	20.5	5.4	7.9	6.7
[illegible]-21*	0.7	0.4	1.2	0.4	1.6	0.4
[illegible]-18	0.2	0.2	0.5	0.2	0.9	0.7
[illegible]	0.1	0.1	0.2	0.1	0.7	0.2

* Sampling periods Oct. 10-16, Oct. 17-23, Oct. 24 - Nov. 6, Nov. 24 - Dec. 7, and Dec. 19 - Jan. 8 are omitted for brevity.

Table 2—Monthly averages of climatic data taken from the experimental area during the study

[illegible]	Climatic parameters				
	Wind	Evaporation	Rain total	Air temperature, °C	
				Max.	Min.
	km/hr	cm/day	cm		
[illegible]	1.65	0.457	0.25	29.9	17.3
[illegible]	1.73	0.243	15.27*	25.7	12.3
[illegible]	2.15	0.183	5.64	22.4	5.2
[illegible]	1.29	0.214	7.65	16.5	2.5
[illegible]	1.27	0.140	4.37	16.7	6.1

* [illegible] cm of rain fell in one storm; the remainder of month was relatively dry.

Volatilization loss expressed as dieldrin flux in grams/ha per day and pounds/acre per day is shown in Fig. 1. Losses were calculated by substituting the atmospheric concentration data from Table 1, assuming a linear concentration gradient between 10 and 30 cm, into equation [1], along with K_p values calculated from equations [2] and [3]. Values of 20 cm and 0.05 cm were used in equations [2] and [3] for z and z_o, respectively. Since z_o was not measured in place, the 0.05-cm value was derived from literature values (Chang, 1968; Priestley, 1959; Sutton, 1953). Undoubtedly, some error was introduced by using atmospheric concentration data and wind speeds time-averaged over periods ranging from 1 to 21 days rather than 15 min to 1 hour. Longer sampling periods were used to ensure that enough dieldrin was trapped at each height to measure the concentration gradient. However, the calculated flux values should be applicable for indicating trends and the magnitude of volatilization. Zero flux values were calculated for the first two sampling periods because of the negative concentration gradients discussed earlier.

Total flux was greatest from the moist soil, where about 18% of the applied dieldrin was lost by volatilization. The peak mean flux rate occurred between 11 and 18 days after application, when more than 6% volatilized in 7 days. Another high flux rate occurred over the moist plot during the sampling period starting on October 3 (Fig. 1). A rainstorm of 15.3 cm at this time appears to have markedly increased the flux rate from the moist plot, compared with only a slight increase in flux rate from the flooded plot and no measureable effect on the nonflooded plot. One could speculate that the 18% vola-

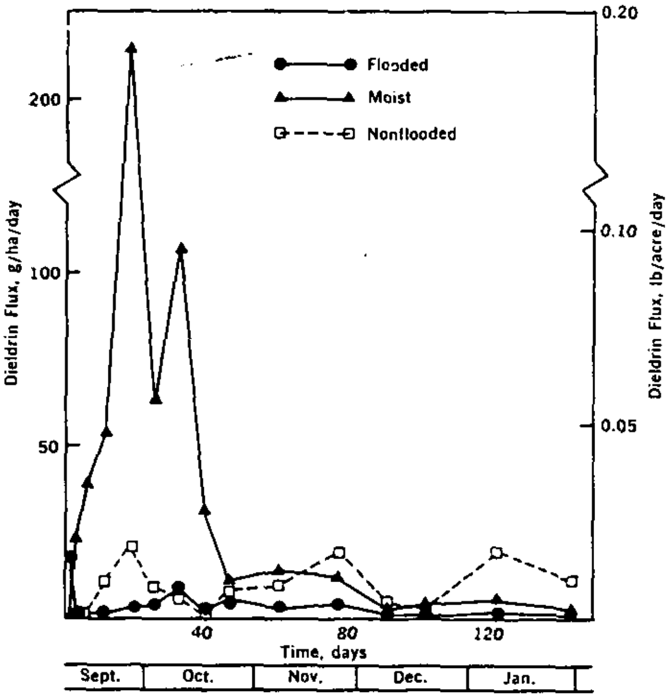

Fig. 1—Effect of different soil water regimes on rate of dieldrin volatilization from fallow plots.

tilization loss of dieldrin from the moist plot might be of similar magnitude under an intensively managed farming operation where frequent irrigation is employed.

Volatilization from the nonflooded plot was relatively low during the first 46 days, but tended to increase with increasing precipitation from November through January, when plot surface conditions (due to rainfall) were similar to those on the moist plot. Also, this increase is probably related to greater residual dieldrin concentrations present on the soil surface because of low volatilization losses during the early stages of the study when the plot surface was relatively dry. However, statistical analysis revealed no significant relationship between rainfall and the rate of flux from the nonflooded plot. The 7% volatilization losses from the nonflooded plot may be similar to losses from nonirrigated land in regions with climatic conditions similar to those of Louisiana.

Flooding appeared to greatly retard the volatilization process, a finding that agrees with previously reported data for DDT (Willis et al., 1971). Only 2.1% of the applied dieldrin was volatilized from the flooded plot. Apparently, dieldrin was sorbed strongly enough by the soil to retard any significant release into the water layer and subsequent volatilization or codistillation from the flooded plot. Average flux rates over the flooded plot were highest during the 1st day, and for the sampling period in early October, when the 13.3-cm rainfall occurred. Again, one could speculate that volatilization losses from the flooded plots might be similar to losses from fields that are flooded as a cultural practice or from swampy areas that are treated with dieldrin.

Multiple regression analysis was used to investigate the influence of climatic parameters (Table 2) and time on the rate of dieldrin volatilization from each of the plots. The following expressions were obtained; those parameters having little relative significance on Y were deleted.

Flooded plot

$$Y = -2.17 + 0.00519\,X_1 + 0.02664\,X_2,\ R^2 = .426$$

Moist plot

$$Y = -3.41 + 0.08836\,X_3,\ R^2 = .282$$

where Y = dieldrin flux, X_1 = time, X_2 = average maximum temperature, and X_3 = average minimum temperature. None of the measured atmospheric variables was significantly correlated with dieldrin flux from the nonflooded plot, although wind approached significance for this treatment.

The relatively low R^2 values indicate that variables other than those measured influenced dieldrin volatilization from the plots. It appears that temperature, not unexpectedly, is an important consideration in dieldrin volatilization. The effect of time is probably related to pesticide concentration at the plot surfaces.

SUMMARY AND CONCLUSIONS

The data indicate that an aerodynamic method has potential for estimating pesticide volatilization losses of [illegible]-applied dieldrin under field conditions. Soil moisture regime has a definite effect on the volatilization rate of this pesticide. Approximately 18% of the applied dieldrin volatilized from a moist plot in 5 months, whereas only and 7% volatilized from flooded and nonflooded plots, spectively. Flooding appeared to greatly retard the vol tilization of surface-applied dieldrin. Volatilization dieldrin from the *nonflooded plot*, although negligi during dry periods, tended to increase with increa precipitation. None of the three soil water regimes any measurable effect on the degradation of soil-inco porated dieldrin, the concentration of which remained same after 6 months. *Of the climatic variables* measu temperature had the greatest effect on rate of volatili tion.

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