

The unexpected effects of the pesticide treatments, relative to that of the control, were not uniform for each of the free sugars. When there was an increase of the concentrations of each of the sugars, that increase was higher for the glucoses and sucrose than for fructose. When the pesticide treatment decreased the sugar concentrations, it was the concentration of sucrose which was the most diminished. The pesticide treatment thus not only changed the concentration of the total of the free sugars but also changed their distribution. As each sugar has its own sweetening power and taste, the pesticide treatment thus could change the taste and thus the quality of the carrot.

Speculations only can be made about the effects observed here of the pesticides on the free sugar concentrations in the carrots. Some remarks, however, may be made.

The active matter of Dosanex is the urea herbicide metoxuron which, like many ureas, inhibits the plant photosynthesis (Corbett, 1974). This could explain the general negative effect of Dosanex on the sugar concentrations.

On the other hand, one knows that the carotenoids contribute to the plant photosynthetic procedures; in photosynthesis, the carotenoids absorb light of wavelengths not absorbed by chlorophylls and pass the energy on to chlorophyll and also protect cell against photosensitized oxidations which otherwise prove lethal to the plant. The functional relationship between sugar photosynthesis and the carotenoids could explain the same direction observed for the pesticide effects on the total carotene and free sugar concentrations (Rouchaud et al., 1982a,b).

The active matters of Dyfonate, Nexion, and Birlane, respectively, are fonofos, bromophos, and chlorfenvinphos, which all are organophosphorus insecticides working on the target insect by inhibiting the acetylcholinesterase. At our knowledge, nothing so far has been reported about the influence of these insecticides, or of their metabolites in

the plant, on the plant sugars and carotenoids syntheses. One remarks, however, that bromophos and chlorfenvinphos have halogenated benzene rings similar to the ones of compounds that interfere with plant growth, like 2,4-D (Thimann, 1951). According to the chemical structure of fonofos, one may speculate that by metabolism in plant it could, proceeding from its ethyl groups, generate ethylene which also is a plant growth regulator.

#### ACKNOWLEDGMENT

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**Registry No.** Birlane, 470-90-6; nexion, 2104-96-3; dyfonate, 944-22-9; afalon spezial, 8000-65-5; dosanex, 19937-59-8; fructose, 57-48-7; sucrose, 57-50-1;  $\alpha$ -glucose, 492-62-6;  $\beta$ -glucose, 492-61-5.

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## Comparative Volatilization and Dissipation Rates of Several Pesticides from Soil

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The volatilization and soil dissipation rates of heptachlor, trifluralin, lindane, heptachlor epoxide, *cis*- and *trans*-chlordane, dieldrin, endrin, DDT, and the isooctyl and propylene glycol butyl ether esters of 2,4-D and 2,4,5-T from fallow soil in microagroecosystem chambers were compared. Volatilization rates of surface-applied pesticides depended upon the vapor pressure of the pesticide. However, changes in volatilization rates immediately after application were nearly the same (ca. 8 h to decline by half) for all pesticides. Volatilization of the higher vapor pressure pesticides (heptachlor, trifluralin, and lindane) was high initially ( $>30 \text{ g ha}^{-1} \text{ day}^{-1}$ ) and decreased rapidly with time, while volatilization of the lower vapor pressure pesticides (dieldrin, endrin, and DDT) was lower initially ( $<10 \text{ g ha}^{-1} \text{ day}^{-1}$ ) and decreased slowly. Both vapor pressure classes were volatilizing at nearly the same rate (ca.  $5 \text{ g ha}^{-1} \text{ day}^{-1}$ ) on day 9, because the amount of pesticide left on the soil surface was about 10% for the volatile pesticides and  $>50\%$  for the less volatile pesticides.

Volatilization is a major dissipation route for many pesticides used in agriculture (Caro and Taylor, 1971; Cliath and Spencer, 1971; Farmer et al., 1972, 1973; Gile

et al., 1980; Harper et al., 1976; Nash and Beall, 1970; Nash et al., 1977; Nash and Woolson, 1968; Spencer and Cliath, 1970, 1972, 1973, 1974, 1975, 1976; Spencer and Farmer, 1980; Spencer et al., 1969, 1973; Taylor et al., 1976, 1977; White et al., 1977; Willis et al., 1971, 1972, 1980). Volatilization seems particularly important for the low vapor pressure, persistent pesticides, such as the chlorinated hydrocarbon insecticides, primarily because small pesticide

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amounts are spread over large surface areas of plant, soil, or water.

Spencer and Cliath (1975, 1976), Spencer and Farmer (1980), and Spencer et al. (1973) have reviewed the literature on volatilization of pesticides from soil. The potential for pesticide volatilization is related to pesticide vapor pressure, but actual volatilization rate is dependent upon the environmental factors that modify or attenuate the effective vapor pressure of the pesticide. The two primary environmental factors affecting volatilization from surfaces are temperature, which influences the vapor pressure, and air movement. When soil moisture decreases on soil surfaces to an amount equal to one monomolecular layer (Spencer and Cliath, 1970; Spencer et al., 1969) amount [Harper et al. (1976) place this at a three molecular layer] the effective vapor pressure and thus volatilization are greatly reduced. Above the monomolecular layer threshold, soil moisture changes have less influence on vapor pressure, though Spencer and Cliath (1974) found that soil moisture contents above the monomolecular layer did have an influence on trifluralin volatilization.

There are several methods for expressing or estimating the dissipation rates of pesticides in the environment. Most of them are empirical. The most common method for expressing dissipation rates of pesticides from soil is to apply the log-transformed exponential equation,  $\ln Y = \ln Y_0 - kt$  (where  $Y_0$  = initial concentration,  $k$  = slope, and  $t$  = time) to a given set of data. The constant ( $k$ ) then simply represents the combined effects of all the environmental variables. Although not precise, the equation gives a good approximation of a pesticide's dissipation rate in the absence of specific environmental data, which is the rule rather than the exception. Nash (1980a,b) has cataloged a large number of  $k$  values describing dissipation from soil for most pesticides under many experimental and environmental conditions.

Pesticides in air can be expressed as concentration ( $\text{g m}^{-3}$ ), and volatilization rate is commonly expressed as flux ( $\text{g ha}^{-1} \text{day}^{-1}$ ) (Harper et al., 1976; Mayer et al., 1974; Spencer and Cliath, 1973, 1974, 1976; Spencer et al., 1973; Taylor et al., 1976, 1977; White et al., 1977; Willis et al., 1972, 1980).

Nigg et al. (1977) suggest that an environmental or weather model  $\ln Y = \ln Y_0 + a_0 \int dt + a_1 \int x_1 dt + \dots + a_n \int x_n dt$  (where  $Y_0$  = initial concentration,  $a_{0-n}$  = coefficients,  $x_{1-n}$  = environmental variables, and  $t$  = time) is the best expression for pesticide dissipation from citrus foliage. Under two different weather conditions, one during a dry, cool period and the other during hot, wet weather, the first-order equation explained only 57% of the variation. When the weather model was used, with cumulative degree days and cumulative rainfall, 94% of the variation was explained.

Walker (1974) has obtained excellent results by using the Arrhenius equation to predict soil-incorporated herbicide persistence. However, for this model, the half-concentration times ( $C_{1/2}$ ) at given soil moistures and temperatures have to be known (usually from laboratory experiments) and field soil (or air) temperatures and moisture contents have to be measured during the period of prediction.

Hartley (1969) and Spencer et al. (1973) have attempted to predict volatilization rates of nonmeasured compounds from nonabsorbing surfaces with the equation  $F_2 = P_2 M_2^{1/2} / (P_1 M_1^{1/2}) \times F_1$  (where  $F$  = flux,  $P$  = vapor pressure,  $M$  = molecular weight, and the subscripts 1 and 2 indicate the reference and unknown compounds, respectively).

This paper reports the comparative volatilization and dissipation of several pesticides applied to a fallow soil surface in chambers during experiments in 1978 and 1979.

## EXPERIMENTAL SECTION

**Conditions.** Both the 1978 and 1979 experiments were conducted in microagroecosystem chambers placed in a greenhouse (Nash and Beall, 1977; Nash et al., 1977). The glass chambers are 150 cm long, 50 cm wide, and 100 cm high above 15 cm of soil. The soil was a sandy loam [(79% sand, 7% silt, and 14% clay) with pH 6.8, organic matter 0.6%, and 33-kPa moisture tension content of 6%] from the University of Maryland's Experimental Farm near Salisbury on the Eastern Shore. The soil was placed in the chambers and moistened several days before treatment on July 31. Sprinkle irrigation (ca 0.44 cm) was provided at 0600 on Aug 1 and 1130 on August 9 for the 1978 experiment. Air temperature (ca. 80 cm above the soil), soil surface and subsurface (ca. 7 cm deep) temperatures, and relative humidity in the chambers were monitored and periodically recorded automatically. Air was pulled through each chamber by a suction fan at a velocity of ca.  $0.08 \text{ m s}^{-1}$ . Volatilized pesticides were trapped on 12 polyurethane air filters (Beall et al., 1976; Billings and Bidleman, 1980; Nash and Beall, 1977; Nash et al., 1977) placed in the air-outlet end of each chamber.

**Treatments.** For the 1978 experiment, commercial formulations of emulsifiable concentrate trifluralin, lindane, and heptachlor (which contained *trans*- and *cis*-chlordane) and pure heptachlor epoxide, additional *trans*-chlordane, dieldrin, endrin, and *p,p'*-DDT (which showed the presence of *p,p'*-DDD) were combined for a single treatment solution (Table I). For the 1979 experiment, pure lindane and heptachlor were added to a combined commercial formulation of emulsifiable concentrate trifluralin and isooctyl esters of 2,4-D for one treatment solution and pure lindane, heptachlor, and dieldrin to commercial trifluralin and the propylene glycol butyl ether esters of 2,4-D and 2,4,5-T as a second treatment solution.

There were five chambers for both experiments. One chamber was used as a control, leaving four replications in the 1978 experiment and two replications for each 1979 treatment. The pesticides were applied by a hand held pressure sprayer, with an attempt to spray the  $0.75 \text{ m}^2$  of the soil surface evenly. Plastic film was placed around the sides of the chamber prior to spraying to prevent chamber side wall contamination. Treatment for both the 1978 and 1979 experiments occurred at ca. 1000 h on July 31.

**Sampling.** Air filters and soil samples (15.1 cm deep by 2-cm diameter cores) were taken periodically throughout both experiments for pesticide assay and determination of soil moisture content. All samples were stored at  $-5^\circ \text{C}$  until assayed. The 1978 experiment covered a period of 10 days. Sampling was extensive during the 24-h periods, July 31 to Aug 1 and Aug 9 to 10. Air samples from two chambers were sampled hourly and the other two chambers bihourly. In addition, the upper three, middle six, and lower three air filters (Nash et al. 1977) were collected for separate analysis.

In 1979, the experiment covered a 3-day period. During ca. a 17-h period on Aug 1 and 2, one air filter from the 12 available in each chamber was collected every 15 min. Each air filter was collected according to a preestablished random selection schedule, which resulted in each air filter being exposed for 3 h except at the beginning or end of the collection period.

**Analytical.** All air filters and soil samples were extracted in a Soxhlet apparatus by using distilled-in-glass organic solvents.

Table I. Common and Chemical Names of Pesticides, Their Application Rates to Surface Soil in Chambers, and Air-Filter Trapping Efficiencies

common	chemical	treatment rate, kg ha <sup>-1</sup>		air-filter efficiency, %
		1978	1979	
<i>trans</i> -chlordane	1,3- <i>exo</i> ,4- <i>endo</i> ,7,8,9,10,10-octachloro-2,3-6,5- <i>endo</i> -tricyclo[5.2.1.0 <sup>2,6</sup> ]dec-8-ene	1		98
<i>cis</i> -chlordane	1,3- <i>exo</i> ,4- <i>exo</i> ,7,8,9,10,10-octachloro-2,3-6,5- <i>endo</i> -tricyclo[5.2.1.0 <sup>2,6</sup> ]dec-8-ene	1.2		94
<i>p,p'</i> -DDD	1,1-dichloro-2,2-bis( <i>p</i> -chlorophenyl)ethane	0.57		79
<i>p,p'</i> -DDT	1,1,1-trichloro-2,2-bis( <i>p</i> -chlorophenyl)ethane	1.7		97
dieldrin	1,8,9,10,11,11-hexachloro-4,5- <i>exo</i> -epoxy-2,3-7,6- <i>endo</i> ,2,1-7,8- <i>exo</i> -tetracyclo[6.2.1.1 <sup>3,6</sup> .0 <sup>2,7</sup> ]dodec-9-ene	2	2	96
endrin	1,8,9,10,11,11-hexachloro-4,5- <i>exo</i> -epoxy-2,1-7,8- <i>endo</i> ,2,3-7,6- <i>endo</i> -tetracyclo[6.2.1.1 <sup>3,6</sup> .0 <sup>2,7</sup> ]dodec-9-ene	2		79
heptachlor	1,3- <i>exo</i> ,7,8,9,10,10-heptachloro-2,3-6,5- <i>endo</i> -tricyclo[5.2.1.0 <sup>2,6</sup> ]deca-4,8-diene	4.2	2	94
heptachlor epoxide	1,3- <i>exo</i> ,7,8,9,10,10-heptachloro-4,5- <i>exo</i> -epoxy-2,3-6,5- <i>endo</i> -tricyclo[5.2.1.0 <sup>2,6</sup> ]dec-8-ene	0.08		105
lindane	$\gamma$ isomer of 1,2,3,4,5,6-hexachlorocyclohexane	0.87	2	86
trifluralin	$\alpha,\alpha,\alpha$ -trifluoro-2,6-dinitro- <i>N,N</i> -dipropyl- <i>p</i> -toluidine	2.8	2	80
2,4-D	isooctyl ester of (2,4-dichlorophenoxy)acetic acid		2.6	62 <sup>a</sup>
2,4-D	propylene glycol butyl ether ester of 2,4-D		2	87 <sup>a</sup>
2,4,5-T	isooctyl ester of (2,4,5-trichlorophenoxy)acetic acid		2	105 <sup>a</sup>
2,4,5-T	propylene glycol butyl ether ester of 2,4,5-T		2	88 <sup>a</sup>

<sup>a</sup> As ester.

**1978 Air Filters.** A few grains of sand plus 125 mL of petroleum ether (30–60 °C fraction) were placed in the bottom Soxhlet flask (Nash et al., 1977). One or two air filters were placed in the Soxhlet and extracted for 2 h. The extract was transferred to a 1000-mL round-bottom flask and the contents were reduced by rotary evaporation. The extract was transferred to a 50- or 100-mL volumetric flask and brought to volume for assay by gas-liquid chromatography (GLC).

**1979 Air Filters.** A few grains of sand plus 100 mL of hexane and 50 mL of methanol plus water (35:15 mL) were placed in the bottom Soxhlet flask. Two consecutively collected air-filters were placed in the Soxhlet and extracted for 5 h. The extracts were placed in a 500-mL separatory funnel and 100 mL of saturated NaCl solution was added. After shaking and separation, the lower aqueous phase was drawn off and saved. The hexane layer was passed through anhydrous sodium sulfate into a 100-mL volumetric flask. The aqueous phase was reextracted with 15 mL of hexane and the hexane transferred to the 100-mL volumetric flask as before. The flask was brought to volume for assay by GLC.

**Soil Samples.** About 1 cm of Florisil and then 5–10 g of weighed soil were placed in a fritted-glass Soxhlet thimble. A small quantity of glass wool was placed on top of the soil to prevent splashing of soil particles. Concurrently, a soil sample was taken for moisture determination. The extraction and subsequent analytical procedure for the soils were the same as for the 1979 air filters.

**GLC Conditions.** Samples were analyzed by <sup>63</sup>Ni electron-capture GLC. The columns were 1.8 m × 4 mm i.d. glass, packed with 3% OV-1 Chromosorb W (AW, DMCS) as primary column or 3% OV-17 Gas-Chrom Q as the secondary column. Column temperature were 220 °C. The carrier gas was CH<sub>4</sub>-Ar (5:95) at a 50 mL/min flow rate. Relative retention times against standards were used for qualitative analyses and peak heights were used for quantitative analyses.

**Air-Filter Trapping Efficiencies.** Air-filter trapping efficiency was determined by using the apparatus described by Beall et al. (1976), which simulated the chamber air-flow rate. Each efficiency trial was for a 24-h period. Trapping

efficiencies for the polyurethane air filters are given in Table I. All experimental data were corrected for both analytical recoveries and air-filter trapping efficiencies for the air samples.

## RESULTS AND DISCUSSION

**Air-Filter Sampling.** Pesticide concentrations in air filters that were sampled at 1 or 2 h and taken from the lower three, middle six, or upper three chamber sections were compared to ascertain the effect of time and position on pesticide trapping efficiencies and quantities. A paired *t* test for daily pesticide means and 59 degrees of freedom (df) indicated no statistical difference between 1- and 2-h air-filter sampling periods as a measure of trapping efficiency. However, the values from the 2-h periods tended to be slightly higher.

When upper, middle, and lower air-filter trap levels were compared in a paired *t* test for pesticide quantities, there were no statistical differences between levels for any of the pesticides, except DDD, for which the middle air filters were significantly higher than the lower air filters at the 95% confidence level. This appears to be an aberration resulting from low DDD concentrations. An important finding in the operation of the microagroecosystem was that no differences in pesticide concentration at the various air-filter trap levels occurred. This means that with fallow soil and 0.08 m s<sup>-1</sup> wind speed, the volatilized pesticide is equally mixed in the air at all levels and no gradients occurred as a result of height above the soil on the air-filter trapping end of the chamber.

**Pesticide Volatilization from Fallow Soil—1978.** Pesticide volatilization flux, soil moisture, soil and air temperatures, and relative humidity are given for days 0–1 and 9–10 in Figure 1. Equations describing the time course of pesticide flux are given in Table II. The decline of pesticide volatilization rate for days 0 and 9 followed an exponential equation quite well for those pesticides with vapor pressures greater than dieldrin but less well for those with vapor pressures less than dieldrin. However, when the equation was limited to the day 0 values the rate of vapor decline ( $-k$ ) for all pesticides was ca. 2. These results demonstrate that under the same conditions and when

Table II. Highly Significant (99% Confidence Level) Exponential Equations Which Describe Pesticide Volatilization (Flux =  $g\ ha^{-1}\ day^{-1}$ ) from Fallow Soil in Microagroecosystem Chambers in 1978

pesticide	vapor pressure, <sup>a</sup> mPa, at 30 °C	day 0	days 0-9	variation accounted for, %
heptachlor	40	$\ln F = 4.8 - 2.55 D^b$	$\ln F = 4.0 - 8.2 D$	87
trifluralin	32.2	$\ln F = 3.9 - 2.61 D$	$\ln F = 3.2 - 6.4 D$	75
lindane	17.04	$\ln F = 3.2 - 2.62 D$	$\ln F = 2.3 - 7.7 D$	85
heptachlor epoxide	2.6	$\ln F = 1.0 - 1.85 D$	$\ln F = 1.5 - 2.4 D$	37
trans-chlordane	1.3	$\ln F = 1.9 - 2.18 D$	$\ln F = 1.3 - 2.7 D$	39
cis-chlordane	1.3	$\ln F = 1.56 - 2.08 D$	$\ln F = 1.0 - 2.3 D$	31
dieldrin	1.3	$\ln F = 1.58 - 1.86 D$		
endrin	0.4 (20 °C)	$\ln F = 1.23 - 1.80 D$		
DDD	0.13	$\ln F = -0.0035 - 1.16 D$		
DDT	0.096	$\ln F = -0.02 - 2.32 D$		

<sup>a</sup> Vapor pressure sources were respectively Bowery (1964), Spencer and Cliath (1973), Spencer and Cliath (1974), estimated, Bowery (1964), Bowery (1964), Spencer and Cliath (1974), Gueckel et al. (1973), Orgill et al. (1976), and Orgill et al. (1976). <sup>b</sup> D = days.

pesticides are applied to a soil surface, the decline in volatilization rate for the first several hours after treatment from a fallow soil is similar for many pesticides. The time required for the volatilization rate to decline to half the initial rate was ca. 8 h (6-9 h) for all pesticides. Only the quantity volatilized differs, which depends upon the vapor pressure (Table II) and amounts available (Table I), trifluralin ( $49\ g\ ha^{-1}\ day^{-1}$ ), vs. dieldrin ( $4.9\ g\ ha^{-1}\ day^{-1}$ ), for example. Spencer and Cliath (1974) found the initial rates of trifluralin volatilization were the same for 1, 2, and 10  $kg\ ha^{-1}$  applications to wet soil surfaces in laboratory studies.

The decrease in volatilization rate for all pesticides on day 0 was rapid until about 1600, when the decrease became less rapid (Figure 1). During the heat of the day the soil surface dried, and then during the night as the soil surface moisture increased, there was a small increase of volatilization relative to early evening hours. Spencer and Cliath (1974) in laboratory studies demonstrated that trifluralin volatilization from soil surfaces was about 100 times greater from wet Gila silt loam than from air-dry Gila soil and that water vapor adsorption on dry soil from 50% relative humidity increased trifluralin volatilization also. Similarly, Harper et al. (1976) in field studies showed that volatilization of trifluralin incorporated into a Cecil soil was low when surface soil water content was low during the day and volatilization increased when the surface soil was rewetted from upward soil water movement during the night. The relative nighttime volatilization increase in this study was more pronounced with the lower vapor pressure pesticides (dieldrin, endrin, and DDT) than with the higher vapor pressure pesticides (trifluralin, lindane, and heptachlor). Similarly on day 1, upon sprinkle irrigation and increased day temperature, volatilization increased, but the increase was far more pronounced for the lower vapor pressure pesticides than with the higher vapor, pressure pesticides. Apparently water is more important in desorbing from soil the lower vapor pressure nonionic pesticides than the higher vapor pressure nonionic pesticides.

The volatilization rate continued to decline on day 9 for the higher vapor pressure pesticides, with only a small increase upon moistening the soil and increased soil temperatures. This results primarily from only 4, 7, and 13% of the original applications left (Table III), respectively, for heptachlor, trifluralin, and lindane. Upon irrigation and increased temperature, considerable volatilization occurred for dieldrin, endrin, and DDT on day 9 relative to day 0, and the peak volatilization was greater than for day 1. Presumably the greater day 9 volatilization was because >50% of the applied dieldrin, endrin, and DDT remained (Table II) and because higher air and soil tem-

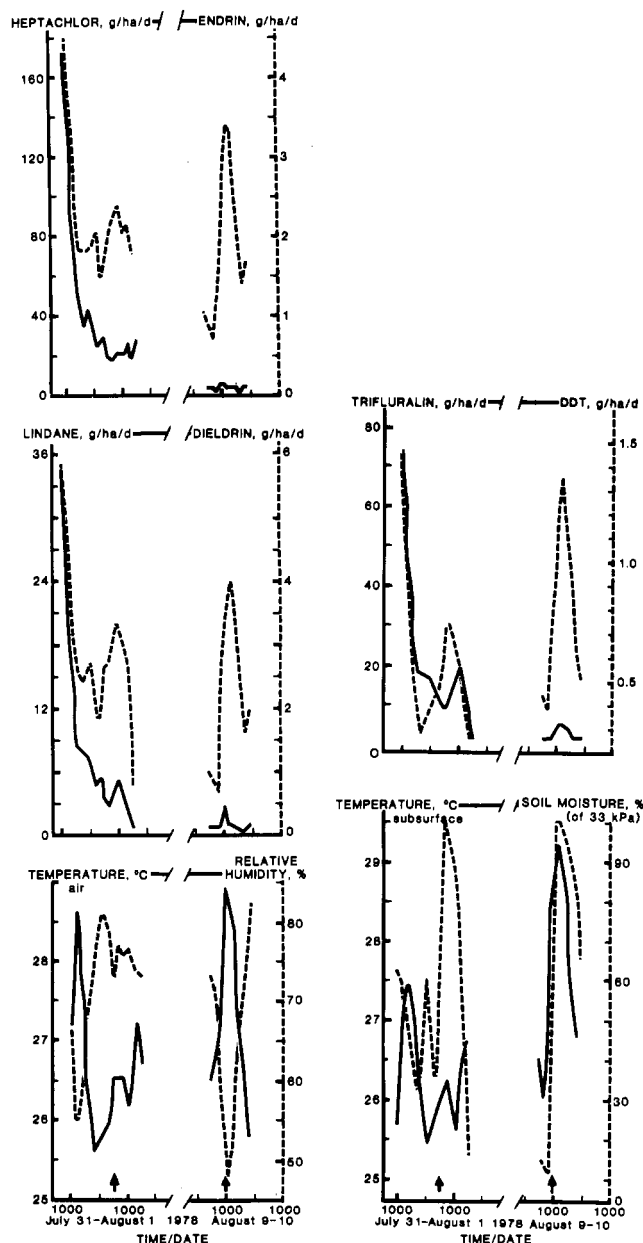


Figure 1. Temperatures, relative humidity, soil moisture, and pesticide volatilization on days 0-1 and 9-10 in chambers. Arrows indicate sprinkle irrigation. Solid and dashed curves refer to left and right vertical axes, respectively.

peratures occurred on day 9 than on day 1. Soil surface moisture, because of sprinkle irrigation (Figure 1), was

Table III. Amount of Pesticide (Percent of Applied Remaining) on Soil Surface in Microagroecosystem Chambers with Time in 1978

pesticide	day							- <i>k</i> <sup>b</sup>	<i>r</i> <sup>c</sup>	- <i>k</i> <sup>d</sup>
	0.065 <sup>a</sup>	0.384 <sup>a</sup>	1.41	2.05 <sup>a</sup>	8.98	9.18 <sup>a</sup>	10.96			
heptachlor	53	62	67	34	5.8	4.2	3.4	0.28	0.99	0.28
trifluralin	72	93	98	51	12	7.3	6.0	0.26	0.98	0.25
lindane	50	75	77	33	17	13	12	0.16	0.95	0.17
heptachlor epoxide	96	112	95	100	65	48	51	0.070	0.95	0.053
<i>trans</i> -chlordane	105	107	98	95	62	55	51	0.068	0.99	0.036
<i>cis</i> -chlordane	110	105	102	106	73	70	60	0.052	0.97	0.036
dieldrin	100	99	95	93	72	72	67	0.036	0.81	0.036
endrin	84	79	78	94	69	72	65	0.021		0.017
<i>p,p'</i> -DDD	83	81	69	80	99	111	186			0.0088
<i>p,p'</i> -DDT	91	91	79	114	126	127	102			0.0072

<sup>a</sup> Three replications; all others four. <sup>b</sup> *k* = slope from exponential equation. <sup>c</sup> Correlation coefficient: 99% = 0.83; 95% = 0.71. <sup>d</sup> Predicted from  $\ln k = -3.49 + 0.61 \ln mPa$  ( $r = 0.99$ ) using heptachlor, trifluralin, lindane, and dieldrin.

Table IV. Balance Sheet from 1978 Microagroecosystem Chamber after 11 Days

pesticide	applied, mg	volatilized <sup>a</sup>		soil surface		total, %
		mg	%	mg	%	
heptachlor	315	188 ± 6.6	59.7	11.7 ± 3.52	3.7	63.4
trifluralin	209	126 ± 12.4	60.3	13.6 ± 3.48	6.5	66.8
lindane	65.4	51.2 ± 9.3	78.3	8.51 ± 1.98	13.0	91.3
heptachlor epoxide	6.02	2.56 ± 0.69	42.5	3.35 ± 0.59	55.6	98.1
<i>trans</i> -chlordane	90.3	45.9 ± 7.3	50.8	50.3 ± 9.82	55.7	106
<i>cis</i> -chlordane	75.2	36.9 ± 11.6	49.1	49.2 ± 9.35	65.4	114
dieldrin	150	53.1 ± 14.2	35.4	110 ± 18.6	73.3	109
endrin	150	49.4 ± 12.9	32.9	105 ± 18.1	70.0	103
<i>p,p'</i> -DDD	43.3	20.3 ± 8.1	46.9	52.9 ± 16.6 <sup>b</sup>	122	169
<i>p,p'</i> -DDT	150	15.8 ± 6.6	10.5	167 ± 28.1	111	121

<sup>a</sup> Corrected for trapping efficiency. <sup>b</sup> After 9 days.

nearly the same for both days 9 and 1.

The vapor losses of the higher vapor pressure pesticides on day 9 were nearly equal to the lower vapor pressure pesticides (heptachlor  $\approx$  endrin, lindane < dieldrin, and trifluralin > DDT) (note the difference in flux scales, Figure 1). Presumably this would continue a few more days until the remaining higher vapor pressure pesticides (heptachlor, trifluralin, and lindane) on the soil surface approached zero. Heptachlor epoxide, and *trans*- and *cis*-chlordane volatilization rates followed similar patterns but were intermediate between the lower and higher vapor pressure pesticides. DDD volatilization followed a pattern similar to DDT.

Six independent variables were measured: relative humidity, subsurface soil, surface soil, and air temperatures, wind speed, and soil moisture. Soil moisture was the most important variable affecting volatilization rate followed by air temperature. Spencer and Cliath (1974) observed that soil moisture content above the monomolecular layer greatly influenced vapor density of trifluralin in Gila silt loam soil but not dieldrin (Spencer et al., 1969) and lindane (Spencer and Cliath, 1970). Statistically, relative humidity, subsurface and surface soil temperatures, and wind speed had little influence on pesticide volatilization. Most likely their nonsignificance was the result of the air temperature accounting for the soil temperature variations (even though air temperatures are primarily influenced by soil temperatures) and because of the rather narrow ranges of variations, i.e., 40–90% RH, 24–30 °C (subsurface), 23–32 °C (surface), and 0.072–0.086 m s<sup>-1</sup> (air movement). Air temperatures ranged from 22 to 33 °C and soil moisture from 9 to 100% of the 33-kPa soil moisture content. Therefore, over short time periods the independent variables needed to describe pesticide volatilization in this study were soil moisture and air temperature.

**Pesticide Persistence on Fallow Soil—1978.** The amount of pesticide remaining on the fallow soil surface

with time is presented in Table III. The first-order equations gave a good description of the pesticide dissipation rates from soil. The more complicated weather model of Nigg et al. (1977) and the Arrhenius equation of Walker (1974) would not appear necessary to describe pesticide dissipation from moist warm soil under the conditions and short period employed in this experiment.

The higher vapor pressure pesticides dissipated at rapid rates during this experiment whereas the lower vapor pressure pesticides dissipated at either much lower or unmeasurable rates. The apparent increase of DDD and DDT with time possibly resulted from errors in extract dilutions which were not necessary for the more volatile compounds.

If volatilization is the major pathway for dissipation of these pesticides from fallow soil, then one can plot (log-log) the rate of soil dissipation (*k*) from the first-order equation vs. their respective vapor pressures and predict the persistence of a similar pesticide, provided the vapor pressure is known (Table III). The predicted *k* values for DDD and DDT were 0.0088 and 0.0072, respectively, which for DDT was not unlike the mean (0.0068) DDT *k* value reported by Nash (1980a) for persistence of DDT on soil surfaces.

**Pesticide Balance Sheet—1978.** A balance sheet of the pesticides was constructed for that volatilized plus that remaining on the soil for the 1978 experiment (Table IV). Nearly all of the pesticides could be accounted for, except heptachlor and trifluralin—the two most volatile pesticides. Even though the values for heptachlor and trifluralin were corrected for air-filter trapping efficiency, nearly 35% was missed in some manner. Possibly some vaporous trifluralin was lost through photodegradation (Ketchersid et al., 1969), and subsequently we have found that about 25% of heptachlor is transformed [apparently to an alcohol (4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methano-1H-inden-1-ol) according to mass spectra data] during 2 h of aqueous heating. The soils were extracted moist and

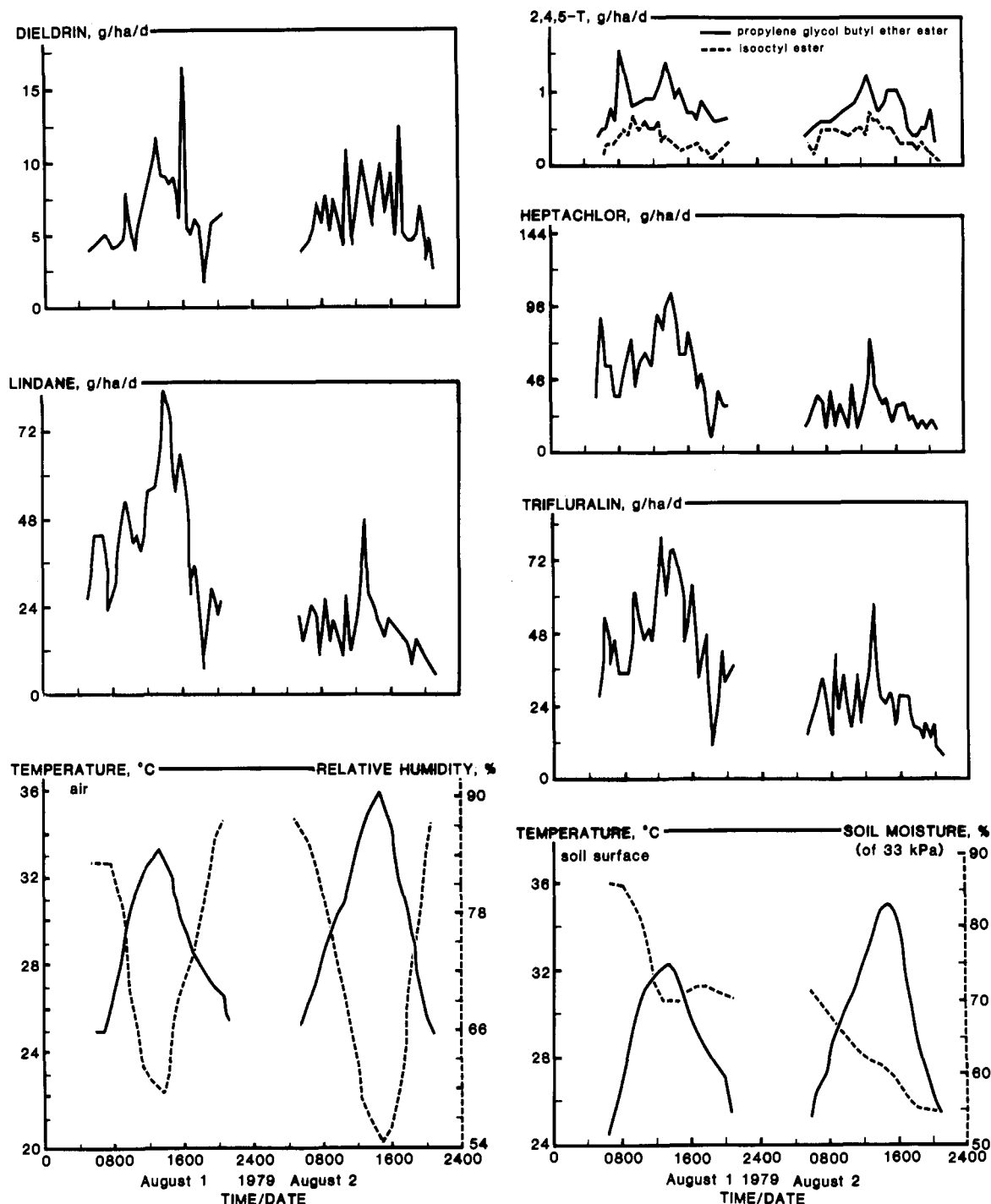


Figure 2. Temperatures, relative humidity, soil moisture, and pesticide volatilization on days 1 and 2 in chambers. Solid and dashed curves refer to left and right vertical axes, respectively, except for 2,4,5-T.

Table V. Highly Significant (99% Confidence Level) Equations Which Describe Pesticide Volatilization (Flux =  $\text{g ha}^{-1} \text{ day}^{-1}$ ) from Fallow Soil in Microagroecosystem Chambers in 1979

pesticide	exponential <sup>a</sup>	stepwise regression <sup>a</sup>	variation accounted for, %
heptachlor	$\ln F = 1 - 0.7 D^b$	$F = 13 - 0.088 \text{ RH} - 2.7 D$	34
trifluralin	$\ln F = 0.7 - 0.6 D$	$F = -2 + 0.25 \text{ SST} - 2.13 D$	27
lindane	$\ln F = 0.7 - 0.8 D$	$\ln F = 3.3 - 0.026 \text{ RH} - 0.81 D$	32
dieldrin		$\ln F = -20 \pm 3 \ln \text{SST} + 1.8 \ln \text{SM}$	12
2,4-D PGBEE <sup>c</sup>		$\ln F = -3 - 0.023 \text{ RH} + 0.03 \text{ SM}$	17
2,4-D IE <sup>d</sup>		$\ln F = -5.8 + 1.8 \ln \text{AT} - 3.9 \ln D$	18
2,4,5-T PGBEE		$\ln F = -3.3 - 1.5 \ln \text{RH} + 1.6 \ln \text{SM}$	13
2,4,5-T IE		$\ln F = -21 + 2 \ln \text{SST} + 1.6 \ln \text{AT} + 1.4 \ln \text{SM}$	53

<sup>a</sup> Days 1 and 2 after treatment. <sup>b</sup> D = day; RH = relative humidity; SST = subsurface soil temperature; AT = air temperature; SM = soil moisture in percent of 33-kPa moisture tension. <sup>c</sup> Propylene glycol butyl ether ester. <sup>d</sup> Isooctyl ester.

Table VI. Amount of Pesticide (Percent of Applied Remaining) on Soil Surface in Microagroecosystem Chambers with Time in 1979

pesticide	day								-k <sup>a</sup>	r <sup>b</sup>
	0	0.63	0.81	0.98	1.6	1.8	1.9	2.2		
heptachlor	67	58	49	43	36	39	39	37	0.28	0.93
trifluralin	79	80	64	61	52	59	55	60	0.17	0.81
lindane	76	78	56	50	66	32	18	32	0.53	0.77
dieldrin	100	98	98	97	96	95	95	94	0.027	0.99
2,4-D PGBEE <sup>c</sup>	116	91	70	78	100	59	50	61	0.29	0.75
2,4-D IE <sup>d</sup>	113	79	88	70		75	51	75	0.22	0.73
2,4,5-T PGBEE	131	121	84	95	100	68	62	74	0.30	0.84
2,4,5-T IE	143	105	111	90		115	74	92	0.18	0.68

<sup>a</sup>  $k$  = slope from exponential equation. <sup>b</sup> Correlation coefficient: 99% = 0.83 and 0.80 and 95% = 0.71 and 0.67 for 7 and 6 df, respectively. <sup>c</sup> Measured as the propylene glycol butyl ether ester. <sup>d</sup> Measured as the isooctyl ester.

water was contained in the extraction solution. On the same soil in the field in 1978, Glotfelty (1981) accounted for 74 and 80% of the initially measured heptachlor and trifluralin, respectively, after 2 days but only 52 and 53%, respectively, of the application.

**Pesticide Volatilization from Fallow Soil—1979.** In the 1979 experiment, no volatilization data were collected for day 0 in order to more precisely measure the influence of the environmental variables on pesticide volatilization (Table V; Figure 2). Volatilization was measured on days 1 and 2 between 0500 and 2200. Volatilization was influenced more by the diurnal variation of days 1 and 2 than by the first volatilization flush after treatment on day 0, the latter being largely dependent upon time (Table II).

Volatilization of the several pesticides in 1979 followed the same patterns as did the 1978 results for days 0–1 and 9–10 (Figure 2). Heptachlor, trifluralin, and lindane (the higher vapor pressure pesticides) volatilization decreased exponentially from day 1 to day 2, while dieldrin and the phenoxy herbicide (the lower vapor pressure pesticide) volatilizations were nearly the same on day 2 as day 1.

The propylene glycol butyl ether ester of both 2,4-D and 2,4,5-T (Figure 2) gave the appearance of being more volatile than the isooctyl ester. Presumably, the isooctyl esters hydrolyzed more rapidly, and hence less ester was available for volatilization.

By limiting the influence of initial volatilization, the importance of the several environmental variables was revealed in stepwise regression equations (Table V). In addition to soil moisture, relative humidity and subsurface temperature increased in importance, whereas air temperature decreased in importance. Presumably, the relationships of relative humidity and air temperature were indirect. Rather, it was the increased midday soil temperatures that increased pesticide volatility through their effect on pesticide vapor pressure. Soil moisture steadily declined during the experiment, but higher soil moisture contents at any given time resulted in a higher flux relative to a lower soil moisture content. Although the stepwise regression equations described the data per se, those for dieldrin and the phenoxy herbicides (except the isooctyl ester of 2,4-D) would have little use for modeling purposes because time was of little or no importance, i.e., flux was constant and the amount lost increased linearly with time.

**Pesticide Persistence on Fallow Soil—1979.** Pesticide persistence on soil was described by the exponential-time equation quite well (Table VI). Stepwise regression analysis of the same data to include the several environmental variables indicated little or no improvement over that provided by the exponential equation in describing persistence of these pesticides on moist fallow soil surfaces. The slopes ( $k$  values) from these first-order equations (Table VI) were similar to those obtained from the 1978 experiment (Table III), except for lindane which

was more than triple the 1979 experiment. The  $k$  values for 2,4-D and 2,4,5-T were for the esters only; therefore, the  $k$  values represent volatilization plus hydrolysis of the esters to their corresponding acids.

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**Registry No.** *trans*-Chlordane, 5103-74-2; *cis*-chlordane, 5103-71-9; *p,p'*-DDD, 72-54-8; *p,p'*-DDT, 50-29-3; dieldrin, 60-57-1; endrin, 72-20-8; heptachlor, 76-44-8; heptachlor epoxide, 1024-57-3; lindane, 58-89-9; trifluralin, 1582-09-8; 2,4-D isooctyl ester, 25168-26-7; 2,4-D propylene glycol butyl ether ester, 1320-18-9; 2,4,5-T isooctyl ester, 25168-15-4; 2,4,5-T propylene glycol butyl ether ester, 62922-39-8.

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## Degradation of Disulfoton in Soil and Its Translocation into Asparagus

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Granular disulfoton at 0.5 and 4.0 kg of a.i./ha was applied as side-dressings to asparagus grown in a sandy loam soil to control the European asparagus aphid, *Brachycolus asparagi*. In soil, disulfoton (DS) oxidized rapidly to its sulfoxide (DSO) and sulfone (DSO<sub>2</sub>), but only minute amounts of the sulfoxide and sulfone of the oxygen analogue (DOASO and DOASO<sub>2</sub>) were present. At the realistic rate of 0.5 kg of a.i./ha the parent compound was detected in soil for about 42 days. Total residues (DS + DSO + DSO<sub>2</sub> + DOASO + DOASO<sub>2</sub>) remained at the level of 1-2 ppm (dry weight) in the side-dress band for about 56 days and decreased to 0.06 ppm in 147 days. In the plants, residues of the sulfoxides and sulfones of both the parent compound and the oxygen analogue were detected after 14 days. However, disulfoton and its oxon were never detected. The total residues (DSO + DSO<sub>2</sub> + DOASO + DOASO<sub>2</sub>) increased steadily to a maximum in about 70-85 days and declined thereafter. After 147 days asparagus ferns from plots treated at 4.0 kg of a.i./ha still contained 17.1 ppm (fresh weight) of total residue. However, only 0.01 ppm of the oxygen analogue sulfone was found in spears collected from the same plots the following growing season. No residue was detected in spears from plots treated at 0.5 kg of a.i./ha. Disulfoton at both application rates reduced the aphid populations to levels below the spray threshold of 0.5 aphid/g of asparagus fern tissue throughout the growing season. No damage in plants was observed in the treated plots whereas the asparagus in the control plots suffered from moderate to heavy damage.

The European asparagus aphid, *Brachycolus asparagi* Mordvilko, is a newly arrived and highly damaging pest of asparagus in the western United States and Canada. A toxin injected by the aphid at feeding causes severe deformity (bonzai or witches' broom-type growth) and even death of the plants (Forbes, 1981). An outbreak of this pest in Washington State and in the Okanagan Valley of British Columbia has been observed since 1979 and has caused considerable economic damage. Currently, malathion, mevinphos, and carbaryl are registered in Canada for control of the asparagus beetle, *Crioceris asparagi* (L.), and the spotted asparagus beetle, *Crioceris duodecimpunctata* (L.). However, they are ineffective against the asparagus aphid because these insecticides act on contact and have short residual activity. In order to suppress the

aphid population throughout the growing season, several applications of these chemicals would be needed. These would probably disturb the balance of the agroecosystem because the chemicals are highly toxic to beneficial insects such as bees and aphid predators, and the applications might cause physical damage to the crop if tractor-mounted boom sprayers were used.

Disulfoton [*O,O*-diethyl *S*-[2-(ethylthio)ethyl] phosphorodithioate, Di-Syston] appeared to us to be a more suitable candidate. It is a widely used systemic insecticide, well suited for the control of sap-feeding insects. The advantage of using this compound is that beneficial insects can forage relatively safely in treated fields because its action is mostly systemic.

This paper describes the translocation of disulfoton and its metabolites from soil to asparagus fern after in-furrow application of Di-Syston 15 G at 0.5 and 4.0 kg of a.i./ha. Also, the efficacy of disulfoton for the control of asparagus aphid is discussed in terms of total residues [disulfoton

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