Fate of Maneb and Zineb Fungicides in Microagroecosystem Chambers

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Maneb and zineb [manganese and zinc ethylenebis(dithiocarbamate)] (EBDC) fungicides were applied twice to tomato plants at 2 kg/ha. The residual fungicides [measured as ethylenediamine (EDA)] and ethylenethiourea (ETU) were monitored on the tomato fruit and leaves and in the soil, water, and air for 100 days after treatment. ETU was detected at <20 ppb on whole fruit after 3 days but completely dissipated after 3 weeks even though maneb and zineb were measurable (as EDA) after 10 weeks. Maneb and zineb were present on whole fruit at <1 ppm. Both had half-concentration times ($c_{1/2}$) of 14 days on leaves. Half-concentration times for ETU, maneb, and zineb on soil were <3, 36, and 23 days, respectively. The $c_{1/2}$ of maneb in air was 7–14 days and that for zineb was 14–11 days as measured by GLC and ^{14}C analysis, respectively. Half-concentration time for ETU in air was 9 days.

Maneb and zineb [manganese and zinc ethylenebis(dithiocarbamate) or EBDC] are two of the most important fungicides for controlling plant diseases (Tweedy, 1973; Engst et al., 1977). Although the EBDC fungicides have been widely used to control plant pathogens for nearly 35 years, their fate and behavior in the environment is not fully understood.

The EBDC fungicides are difficult to study in the laboratory or environment since no good analytical procedure has been developed for assaying the parent EBDC or many of their degradation or conversion products. Fortunately, most of the conversion products are labile in the environment. Analytical procedures for measuring minute quantities of the EBDC fungicides usually involve chemically fracturing the parent molecule, then measuring the component, i.e., CS_2 or ethylenediamine (EDA) (Keppel, 1971; Newsome, 1976), or using ^{14}C-labeled fungicides, then measuring the ^{14}C (Nash, 1976; Vonk, 1975). In addition, fungicides containing manganese and/or zinc are very water insoluble. Thus, only a few researchers (Engst et al., 1977; Hoagland and Frear, 1976; Newsome, 1976; Newsome et al., 1975; Pease and Holt, 1977; Ripley, et al., 1978; Vonk, 1975, 1976, and their co-workers) have partially elucidated the nature of the EBDC fungicides and their degradation or conversion products in the environment.

The major concern about using the EBDC fungicides is the presence or potential conversion of EBDC fungicides to ethylenethiourea (ETU) (2-imidazolidinethione). Several toxicological studies indicated that ETU was toxic to rats (Graham et al., 1973; Meland et al., 1972) and mice (Innes et al., 1969; Khera, 1973).

Nash (1976), Newsome (1976), Newsome et al. (1975), Pease and Holt (1977), Ripley et al. (1978), and Vonk (1975) and co-workers have all studied the presence or fate of EBDC fungicides and ETU on various fruits, vegetables, and crops. They generally agreed that ETU is formed during the dissipation of the EBDC fungicides and that the conversion rate or degradation of ETU is greater than its formation rate; hence, no ETU accumulates on fruits, vegetables, or in any portion of the environment.

To further verify the nature of the EBDC fungicides and ETU in the total environment, we conducted an experiment in microagroecosystem chambers (Beall et al., 1976), which allow us to follow the fate of a pesticide in the total environment; i.e., plant, soil, water, and air.

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EXPERIMENTAL SECTION

Materials. The experiment was conducted from 26 April 1976 to 4 August 1976 in a greenhouse where our five microagroecosystem chambers (enclosed glass chambers) (150 × 115 × 50 cm) (Nash et al., 1977) with air filters are housed. Air is drawn through the chambers for cooling, and after filtering the outlet air, the pesticide concentration in the air can be determined from extracts of filters.

The soil used was a Galestown sandy loam (Psammentic Hapludults) with a pH value of 6.7, organic matter content of 5.2%, and 1/3 bar moisture tension at 15.6% soil water content. The soil was fertilized with 100 kg/ha of nitrogen from a 10–10–10 NPK nitrogen, phosphorus, and potassium fertilizer. Sprinkle irrigation was provided as needed.

Five 19-day-old tomato (*Lycopersicon esculentum* Mill. cv. Rutgers) plants were transplanted into each chamber. At day 56 and 86, the tomato plants were sprayed with Manzate D (maneb) and Zineb W75 (zineb) fungicides at 2 kg of active ingredient/ha. However, the second application (day 86) contained 180 μCi of [^{14}C]maneb (5.98 μCi/mM) or 120 μCi of [^{14}C]zineb (7.14 μCi/mM) per chamber, also. Both were labeled in the 1,2-ethylene position. The maneb and zineb treatments were applied to plants in duplicate microagroecosystem chambers, while the remaining chamber was used as a control.

Prior to fungicide application, 120 microscope glass slides were adhered to the inside chamber walls with a small amount of caulking compound. Likewise, prior to fungicide application, 20 glass slides were placed on the soil surface and were collected right after fungicide application.

Sampling. Periodically the tomato fruit (after day 86) and leaves, soil, leachate water, air, and glass slides from chamber walls were sampled (Nash et al., 1977) to determine maneb, zineb, and ETU concentrations. The air sampling was by periodic exchanging of polyurethane foam filters (Beall et al., 1976), which continuously trapped the volatilized maneb, zineb, and ETU. The tomatoes were peeled by hand and only the peels were analyzed. At the end of the experiment, the tomato plants and plant residues on the soil surface were removed from the chamber, weighed, sampled, and analyzed.

Air Filters Trapping Efficiency. In a separate experiment, the efficiency of the air filters (5 cm thick × 5 cm diameter plugs of polyurethane foam) for trapping EBDC, ETU, and their conversion products was determined by placing a known quantity of ^{14}C-labeled maneb,

zineb, or ETU on fiberglass cloth and drawing air through the cloth and filter by using a special glass thimble (Beall et al., 1976). These filters were collected (or changed) after 0.02, 0.13, 1, 3, and 7 days for the first test; 0.02, 0.13, 1, 3, 7, 14, and 21 for the second; and 0.08, 0.25, 1, 2, 4, 7, 14, and 28 days for the third test. At the end of each test, the fiberglass cloth was also collected for analysis to determine how much EBDC and ETU remained on the cloth.

Analyses. *Fungicides.* The fungicides (as ethylenediamine, EDA) were determined similar to the procedure of Newsome (1974), except a pentafluorobenzylated derivative was formed.

Samples of soil (<7 g), chopped plant leaves, or tomato peels (ca. 10 g) were refluxed with 25 mL of freshly prepared stannous chloride in 1 N HCl (1 mg $SnCl_2$/mL) for 1 h to convert the fungicide and its ethylenediamine metabolites to EDA. An ion-exchange column was prepared by (1) placing ca. 2.4 cm^3 of Dowex 50W-X8 (20–50 mesh, sphericity >85%) in a stopcock column, (2) eluting the column slowly with 15 mL of water, (3) eluting the column slowly with 15-mL 1 N HCl, and (4) eluting the column slowly with 4 × 5 mL of water.

The refluxed sample was filtered after it was cooled, and the filtrate was placed on the column and allowed to slowly pass through. After the filtrate had passed through the column, 15 mL of 1 N NaCl was added to the column in 5-mL increments and allowed to pass through. The stopcock was closed and 1 mL of saturated $NaHCO_3$ added. After ca. 2 min, the stopcock was opened and additional $NaHCO_3$ was added until 5 mL of eluate was collected.

Air filters and fiberglass cloth (first two tests) were Soxhlet extracted with 100 mL of hexane + 35 mL of methanol + 15 mL of water for 5 h. The two phases were separated in a 250-mL separatory funnel, and the lower aqueous layer was saved in a 250-mL, round-bottom flask. The Soxhlet flask was rinsed with 25 mL of methanol and the rinse was placed in the separatory funnel. The hexane was reextracted and the lower layer drawn off into the previous aqueous phase. The contents of the round-bottom flask were reduced to <50 mL on a rotary evaporator, transferred to a 50-mL flask, and brought to volume. A 25-mL aliquot was taken for conversion to EDA, as previously described.

A 500-mL aliquot of water was taken from 1–2 L of leachate from the microagroecosystem chamber and reduced to <50 mL on a rotary evaporator. The contents was transferred to a 50-mL flask and brought to volume, and 25 mL was taken for EDA analysis, as previously described.

Subsamples of the 5 mL of eluate from soil, air, water, and tomato fruit (two 100-μL aliquots) and leaves (25- and 50-μL aliquots) of the $NaHCO_3$ eluate were transferred to a pointed glass-stoppered test tube. Concentrated HCl (one drop) was added, and the contents was vigorously shaken. The test tube was placed in a vacuum desiccator containing NaOH pellets.

After the samples were desiccated, the contents of the pointed tube was further dried with dry N_2, 1 mL of 0.5% pyridine in hexane was added, and the contents was shaken and allowed to stand ca. 5 min. Within 5 min, 2 mL of 1.25% pentafluorobenzoyl chloride in hexane was added, and the contents was shaken. About 1 mL of 0.3 N KOH and one drop of pyridine was added, and the pointed tube was shaken and allowed to stand. The product ratio changes with time; hence, it was necessary to complete the above steps in <5 min. Over the next several minutes, the pointed tube was alternately shaken and allowed to stand until the emulsion had cleared.

Two of the three milliliters of the EDA derivative was placed on a previously prepared mini Florisil column (0.8 g in a disposable Pasteur pipet, capped with anhydrous Na_2SO_4, placed in a 130 °C oven overnight, then taken from the oven and cooled) attached with Teflon tubing to a short stem funnel. The funnel was rinsed twice with 1 mL of hexane and followed with 5 mL of hexane. The receiver was changed and the hexane eluate discarded. The column was eluted with 10 mL of 2% methanol in benzene (v/v). The eluate was assayed for the EDA derivative by gas–liquid chromatography (GLC) and liquid scintillation counting.

Efficiency of recoveries for EDA were determined by adding various amounts of EDA to a subportion of control sample, except air-filter samples in which case a separate set of air filters were used. Hence, each set of samples contained an analytical efficiency of recovery sample. The efficiency of recovery in percent for the above procedures for EDA were tomato leaves, 58 ± 16; soil, 25 ± 6; and air filters, 58 ± 19.

Glass slides and fiberglass cloth (third test) were rinsed with methanol/water (1:1), then with hot 1 N HCl. After taking 5 mL of the methanol/water rinse for ETU analysis, the remainder was combined with the acid rinse. EDA was analyzed as previously described.

ETU. ETU was determined according to the 2-(*o*-chlorobenzylthio)-1-(pentafluorobenzoyl)-2-imidazoline derivative procedure (Nash, 1975) immediately after sampling. Mean recoveries were >95% (103 ± 10% for leaves, 97 ± 6% from soil, and 95 ± 2% for air filters). About 10 g of soil, tomato leaves, or peels was homogenized with 20 mL of methanol, filtered, and rinsed with additional methanol to a final volume of 50 mL. Then 10 mL of the methanol extract was diluted with 10 mL of water, four drops of *o*-dichlorobenzyl chloride was added, and the contents was refluxed for 30 min.

For air filters and leachate water samples, 10 mL of the extract was diluted with 10 mL of methanol before refluxing. For glass slides, 5 mL of methanol/water extract was diluted with an additional 5 mL of methanol and 10 mL of water.

After the contents was cooled, the refluxed extract was placed in a 250-mL separatory funnel that contained 5 mL of 0.2 N HCl, 25 mL of water, and 10 mL of $CHCl_3$. The funnel was shaken and the lower $CHCl_3$ phase discarded. Then 10 mL of $CHCl_3$ and 10 mL of 1.5 N KOH were added, and the funnel was shaken immediately for 15 s. The lower chloroform phase was passed through anhydrous Na_2SO_4 into a 15-mL pointed test tube. Another 5 mL of $CHCl_3$ was added to the funnel, the funnel was shaken, and the contents was combined with the former. One drop of castor oil was added to the chloroform, and the contents was shaken. The $CHCl_3$ was gently blown off with dry N_2 by placing the tube into a tube heater at 33–40 °C. From 0.5 to 1 mL of 1% pentafluorobenzoyl chloride in hexane and one drop of 0.1% pyridine in hexane were added to the residue in the pointed test tube. The contents was shaken and the tube placed in the tube heater at 65 °C for 15 min.

Contents of the pointed test tube was placed on a mini Florisil column (previously described) that was cooled and wetted with hexane. The tube was then rinsed three times with 1 mL of hexane and the rinse placed on the column. The column was eluted with 5 mL of benzene and the eluate discarded. Finally, the column was eluted with 10 mL of 2% methanol in benzene. The eluate was shaken and assayed for the ETU derivative by GLC and liquid

Table I. Concentration of Maneb and Zineb Measured as Ethylenediamine (EDA) and ETU on Fresh Tomatoes Grown in Microagroecosystem Chambers

	compound							
	[^{14}C]EDA				ETU			
	peel				peel (GLC)		whole tomato	
	extracted		non-extracted,	whole tomato,				
day	ppm	$\mu g/cm^2$	ppm	ppm	ppb	ng/cm^2	GLC, ppb	^{14}C, ppb
				maneb				
86	1.08 ± 1.40[a]	1.61	0.02	0.07	5	7	0.3	0.8
89	5.13 ± 2.60	10.45	0.02	0.28	245	500	13.3	3.6
98	1.05 ± 0.79	1.03	0.03	0.13	119	116	15.1	16.7
99	0.58 ± 0.27	0.62	0.02	0.06	3	3	0.3	1.3
107	0.37 ± 0.25	0.86	0.03	0.03	2	5	0.2	0.2
114	0.88 ± 0.15	2.53	0.15	0.06	ND[b]			ND
128	1.23 ± 0.37	1.18	0.02	0.12	ND			1.3
156	1.26 ± 0.97	1.50	0.03	0.03	ND			ND
				zineb				
86	1.44 ± 0.01	3.54	0.03	0.21	2	2	0.2	4.3
89	7.43 ± 2.25	14.95	0.04	1.05	14	27	2	5.0
98	1.63 ± 0.54	1.67	0.02	0.38	4	4	1	14.4
99	0.64 ± 0.13	0.49	0.01	0.20	ND			3.5
107	1.87 ± 1.73	0.49	0.02	0.30	3	8	0.5	4.2
114	1.21 ± 0.13	2.61	0.25	0.14	ND			0.5
128	1.49 ± 0.16	1.44	0.01	0.30	ND			0.2
156	0.82 ± 0.10	0.96	0.02	0.19	ND			ND

[a] Mean and standard deviation. [b] None detected.

scintillation counting (Nash, 1975, 1976).

GLC. GLC analyses were conducted using a ^{63}Ni electron-capture detector. Glass columns (1.8 m × 4 mm i.d.) were packed with 3% XE-60 Chrom W (AW-DMCS), 80–100 mesh, and 3% OV-17 Gas-Chrom Q, 100–120 mesh (column temperatures of 220 and 210 °C, 5% CH_4 in argon flow of 50 and 75 mL/min, respectively) as primary and secondary columns for ETU analyses, respectively. EDA primary and secondary columns were 3% OV-17 Gas-Chrom Q and 3% OV-1 Chrom W (AW-DMCS), 80–100 mesh (column temperatures, 205 and 215 °C; gas flow, 80 and 50 mL/min, respectively).

Combustion. Subsamples of tomato leaves and extracted leaves, tomatoes, and soils and whole extracted fiberglass cloth were combusted in an automatic oxidizer. The $^{14}CO_2$ was collected for liquid scintillation counting.

Mass Spectra. High-resolution mass spectra of the EDA derivatives were obtained with a DuPont 491B mass spectrometer. Samples were analyzed via direct probe with a source temperature of 235 °C.

Definition. The term *half-concentration time* ($c_{1/2}$) refers to the time required to reduce the maximum chemical concentration by one-half in an environmental component. In this paper, the first-order rate equation was used to determine $c_{1/2}$ in days. Maximum chemical concentration is at time zero, unless otherwise noted.

RESULTS AND DISCUSSION

Ethylenediamine Pentafluorobenzoylation. The isobutane chemical ionization mass spectrum for the product of the pentafluorobenzoylation of ethylenediamine (EDA) [bis(pentafluorobenzoylamino)ethane] was dominated by the protonated molecular ion at m/e 449, 100%. The molecular mass of 448 was further confirmed by the presence of alkyl adduct ions at m/e 489, 6% $(M + C_3H_5)^+$ and m/e 491, 1.5% $(M + C_3H_7)^+$. Low abundance fragment ions occurred at m/e 238, 237, 225, and 195. The melting point was 259 °C, with possible decomposition. We found that under our analytical conditions of EDA derivatization, another derivative was formed with a GLC retention time of ca. 0.7 of the primary derivative. This was controlled by maintaining the pentafluorobenzoylation reaction time to less than 5 min.

Table II. Comparison of Methods for Determining ETU and EBDC Fungicides in Vegetables

	ETU, ppm		EBDC, ppm	
vegetable	PDL[a]	EPA[b]	PDL	EPA
carrots				
raw	<0.002	<0.01	0.08	0.1
canned	<0.002	0.01	0.23	0.1
spinach				
raw	0.26	0.33	3.53	0.6
raw	0.07	0.01	0.22	5.5
canned	0.17	0.14	0.33	0.1
canned	0.68	0.53	0.63	0.1
tomato				
raw	<0.002	NI[c]	0.07	NI
canned	0.07	0.01	0.65	0.4
canned	0.05	0.05	0.53	0.1

[a] Pesticide Degradation Laboratory, U.S. Department of Agriculture. [b] Environmental Protection Agency. [c] Sample not identified.

Tomato Fruit. The concentration of maneb and zineb on the peel and whole tomato fruit with time are given in Table I. Since the fruit was hand-peeled, tomato meat was often attached to the peel, which would increase peel weights over those peeled commericially. Hence, possibly greater concentrations of fungicide would be found than those given in Table I.

For maneb and zineb determined as the [^{14}C]EDA, losses of either fungicide on the fruit were not discernible. However, the amounts present at any given time were low (<0.4 ppm on whole fruit, except for zineb on day 89).

By both ^{14}C and GLC analyses, ETU was detectable in the ppb range on tomato peel until after 13 days (day 99) when little was detectable. After 21 days (day 107), none was detected. There seemed to have been a possible buildup of ETU initially, but the sprinkle irrigation on day 98 apparently washed the ETU off the fruit. After that the loss rate of ETU exceeded its formation rate. Apparently ETU dissipated similarly from tomato fruit for both maneb and zineb.

Recovery of EBDC from tomato peel was poor and variable. Nevertheless, the procedure appeared better than

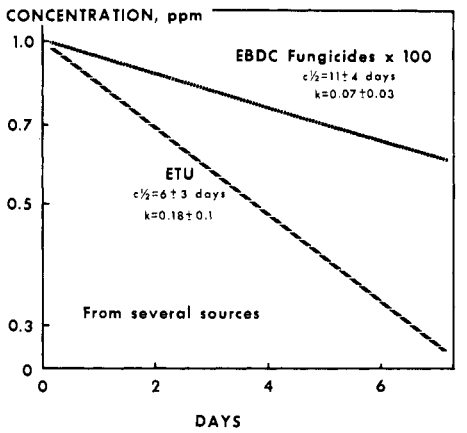

Figure 1. Dissipation of EBDC fungicides and ETU from several vegetables.

a CS_2 method (Barron, 1976). Table II compares the ETU and EBDC values obtained by our laboratory and those furnished by the U.S. Environmental Protection Agency on vegetables. Our EBDC values were higher, except for one sample (0.22 vs. 5.5 ppm) which was unusually high. However, the EPA EBDC values appear low because both their canned spinach values contained ETU amounts greater than the EBDC amounts. Both methods for EBDC include ETU as well; hence, the EBDC amount should always be equal to or greater than the ETU amount.

Table III lists the dissipation rate and $c_{1/2}$'s of several EBDC fungicides and their conversion products, ETU and 5,6-dihydro-3*H*-imidazo[2,1-*c*]1,2,4-dithiazole-3-thione (DIDAT), determined from results found in the literature. The dissipation rate was determined from the first-order equation $\ln c_t = \ln c_o - kt$; where c_o = concentration at t_o, and k = dissipation rate in days. Figure 1 presents a scheme of these results.

The $c_{1/2}$ values of the EBDC fungicides on fruit and vegetables range from 3 to 35 days, with an average of 7 to 11 days. The $c_{1/2}$ of ETU ranged from 3 to 28 days, with a mean of 6 days. DIDAT (formerly known as ethylenethiuram monosulfide) had a $c_{1/2}$ value of 3 days.

Tomato Leaves. Unlike fruit concentrations, small amounts (<0.5 ppm) of ETU were found on the leaves throughout the experiment (Table IV). Possibly ETU formed on the leaves and was maximum at about 14 days (days 71 and 99) after spraying. After sprinkle irrigation, at days 72 and 98, the ETU loss rate exceeded its formation rate for the first and second application, respectively.

The presence of ETU for a longer time on leaves than fruit probably reflects the greater amounts and persistence of the fungicide present on the leaves. Concentrations of EDA were detectable by both GLC and ^{14}C throughout the experiment. The greater amounts of fungicide on the leaves during the first treatment reflects the small size of the tomato plants compared with those during the second treatment (Table IV). The large standard deviation for EDA during the first treatment possibly resulted from sampling the leaves while they were still dripping with the spray application, in addition to inadequate sampling. The $c_{1/2}$ value for both maneb and zineb on tomato leaves was 14 days (Figure 2).

Soil. Soil concentrations of ETU were detectable by GLC measurement only during the first 2 days (days 26 and 88) after treatment for both maneb and zineb (Table V). The ETU measured by ^{14}C may or may not have been ETU because it is possible some other ^{14}C conversion product like ethyleneurea might have survived the ETU derivatization and cleanup process (Nash, 1976).

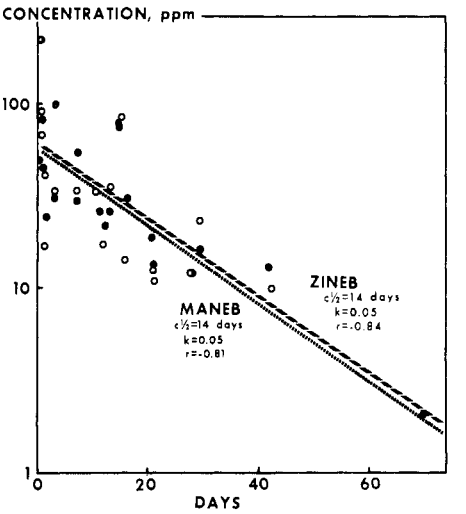

Figure 2. Dissipation of maneb and zineb from leaves of tomatoes grown in microagroecosystem chambers.

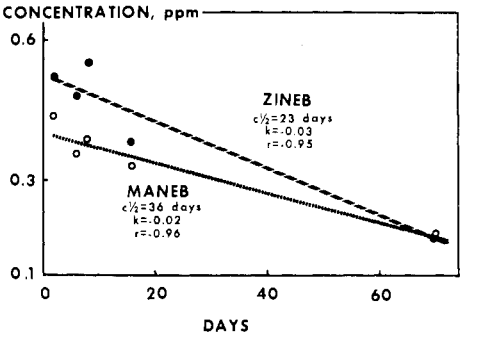

Figure 3. Dissipation of maneb and zineb from 1-cm surface soil in microecosystem chambers.

Like EDA on tomato leaves, EDA was present on the soil surface throughout the experiment (Figure 3). Clearly, little maneb or zineb or their possible degradation products moved within the soil (Table V). Also, none was found below 1 cm, or possibly even below 1 mm.

Results for EDA and ETU on soil for the first treatment are not presented because we found ETU only on the glass slides, and we had considerable difficulty in analyzing the soils for EDA initially. The hot HCl digestion of the soils resulted in solubilizing considerable amounts of iron. Consequently, when the digest was placed on the ion-exchange column, the iron presumably covered many of the adsorptive sites and reduced the column's capacity to adsorb EDA. In addition, when the ion-exchange column was made alkaline, the iron precipitated and possibly affected the results. This problem was overcome by keeping the soil sample weight below ca. 7 g and allowing adequate time for the resin to adsorb the EDA.

Leachate Water. No ETU was found in the water from the first treatment, but the amount (<0.5 μg/L) found in the leachate from the second zineb treatment was nearly the same order of magnitude as EDA when measured by GLC (Table VI). ETU is water soluble and would be expected to move more rapidly in soil than the parent fungicides. The amount of ^{14}C equivalent to maneb or zineb was much greater (34–40 μg/L), which indicated some soluble degradation products, but presumably not products which could be measured as EDA.

Air. Air concentrations of maneb (<10 ng/m^3) or zineb (<20 ng/m^3) as EDA found in air by GLC were lower than the amounts of maneb (<100 ng/m^3) and zineb (>200 ng/m^3) measured by ^{14}C (Figure 4). The large discrepancy between the two values presumably resulted from ^{14}C

Table III. Dissipation Rates (k in Days) and Half-Concentration Time ($c_{1/2}$ in Days) of the EBDC Fungicides and Their Conversion Products ETU and DIDAT

plant	conditions	$-k$	$-r^a$	$c_{1/2}$	ref
		Maneb			
beans	spray	0.105	0.99	6.4	Newsome et al., 1975
tomatoes	spray	0.094	0.93	7.4	same as above
tomato leaves	spray	0.048	0.81	14	this study
		Mancozeb			
apples	spray	0.050	0.99	14	Wood in Engst et al., 1977
		Manzate			
squash	spray	0.160	0.79	4.3	Pease and Holt, 1977
		Manzate 200			
squash	spray	0.211	0.69	3.3	same as above
		Manzate D			
tomatoes	spray	0.095	0.86	7.3	Newsome, 1976
cucumbers	spray	0.211	0.70	3.3	Pease and Holt, 1977
squash	spray	0.204	0.76	3.4	same as above
cantaloupe	spray	0.219	0.66	3.2	same as above
		Dithane			
tomatoes	spray	0.113	0.76	6.1	Newsome, 1976
		Polyram 80-W			
tomatoes	spray	0.111	0.97	6.2	Newsome, 1976
apples	spray	0.080	0.99	8.7	Wood in Engst et al., 1977
	mean	0.13 ± 0.06		7 ± 4	
		Zineb			
tomatoes	spray	0.099	0.87	7.0	Newsome, 1976
lettuce	small droplets	0.064	0.93	11	Vonk, 1976
grapes	spray	0.020	0.66	35	Ripley et al., 1978
tomato leaves	spray	0.048	0.82	14	this study
	mean[b]	0.07 ± 0.03		11 ± 4	
		ETU			
tomato	injected	0.073	0.99	9.5	Hoagland and Frear, 1976
pepper	injected	0.058	0.96	12	same as above
bean	injected	0.155	0.96	4.5	same as above
pepper	excised leaves	0.194	0.98	3.6	same as above
tomato, lettuce, corn	excised leaves	0.282	0.96	2.5	same as above
grapes	spray	0.025	0.82	28	Ripley et al., 1978
tomatoes	dithane spray	0.111	0.89	6.2	Newsome, 1976
tomatoes	manzate spray	0.089	0.91	7.8	same as above
soybeans	manzate spray	0.401	0.98	1.7	Nash, 1976
soybeans	manzate spray	0.060	1.00	12	same as above
soybeans	nabam spray	0.179	0.97	3.9	same as above
soybeans	maneb spray	0.248	1.00	2.8	same as above
soybeans	zineb spray	0.205	1.00	3.4	same as above
tomatoes	maneb spray (1st 6 days)	0.310	0.98	2.2	Newsome et al., 1975
beans	maneb spray	0.159	0.93	4.4	same as above
tomatoes[c]	maneb spray	0.243	0.76	3	this study
tomatoes	zineb spray	0.077	1.00	9	same as above
	mean[b]	0.18 ± 0.1		6 ± 3	
		DIDAT			
tomatoes	manzate D	0.178	0.87	3.9	Newsome, 1976
tomatoes	maneb spray	0.253	0.82	2.7	Newsome et al., 1975
beans	maneb spray	0.354	0.89	2.0	same as above
	mean	0.26 ± 0.09		3 ± 1	

[a] r = correlation coefficient. [b] Excludes grapes. [c] GLC values beginning with 89th day.

products not measured as EDA. We assumed the EDA analytical procedure was valid because of our consistent recoveries of 58% from the filters, like that for the tomato leaves, and because the recovery values for the tomato leaves for both GLC and ^{14}C do not show this wide range of difference.

Compared with the treatment solutions as measured by GLC, the amounts of ETU in air relative to EDA for maneb or zineb were greater, which indicated ETU is more volatile than maneb or zineb (Figures 4 and 5). The treatment solutions contained 1.13 ± 0.24% and 1.59 ± 0.23% ETU for maneb and zineb, respectively, whereas ETU constituted nearly 10% of the total voltalized compounds. By ^{14}C measurement, the ETU in air was of the same order of magnitude as by GLC. However, ETU measured as ^{14}C relative to EDA measured as ^{14}C was more nearly like the treatment solutions. Therefore, this suggests that much of the ^{14}C was other volatile compounds and not maneb, zineb, or compounds that could be measured as EDA.

Between the 7th and 21st day after treatment ETU concentrations in air seemed to decrease rather sharply, especially the GLC values. Possibly, sprinkler irrigation on days 71 and 98 (15 and 12 days after treatment), which reduced ETU levels on tomato fruit and leaves, reduced the ETU air concentrations also.

Chamber Walls. At the time of the second fungicide application (day 86), the tomato plants were large, filling most of the chamber. Consequently, nearly 20% of the application was found on the chamber walls (Figure 6). The ^{14}C seemingly dissipated rapidly from the chamber walls, with ca. 0.1 of that initially present remaining after 14 days (day 100). However, these losses were not reflected by the amount of fungicide found in the air. Of the total

Table IV. Concentration of Maneb and Zineb Measured as Ethylenediamine (EDA) and ETU in/on Fresh Tomato Leaves of Plants Grown in Microagroecosystem Chambers

	compound									
	EDA							ETU		
			^{14}C							
	GLC		total		extracted		non-extracted,[a]	GLC		
day	ppm	$\mu g/cm^2$	ppm	$\mu g/cm^2$	ppm	$\mu g/cm^2$	ppm	ppm	ng/cm^2	^{14}C, ppm
					Maneb: First Treatment					
56	228 ± 339[b]	5.4						0.1 ± 0.04	2.4	
56.3	89 ± 36	2.1						0.05 ± 0.05	1.2	
57	41 ± 11	0.98						<0.01	<0.1	
60	96 ± 37	2.4						0.02 ± 0.03	0.5	
63	34 ± 22	0.88						0.04 ± 0.03	1.0	
67	33 ± 20	0.89						0.25 ± 0.04	6.8	
71	84 ± 40	2.3						0.11 ± 0	3.0	
72	24 ± 8	0.68						0.21 ± 0.03	6.0	
77	11 ± 7	0.31						0.23 ± 0.06	6.0	
85	23 ± 28	0.60						0.01	0.1	
					Maneb: Second Treatment					
86	68 ± 17	2.0	58 ± 33	1.7	44 ± 42	1.3	15 ± 7	0.02 ± 0.02	0.6	1.16 ± 0.25
87	17 ± 4	0.50	47 ± 16	1.4	30 ± 65	0.88	15± 13	<0.01	<0.3	0.26 ± 0.05
89	34 ± 0	1.0	26 ± 6	0.77	18 ± 3	0.53	5 ± 1	0.18 ± 0.14	5.3	1.82 ± 0.85
93	33 ± 18	0.97	22 ± 2	0.63	13 ± 3	0.38	4.1	0.11[c]	3.2	0.68 ± 0.04
98	17 ± 11	0.50	47 ± 30	1.4	37 ± 42	1.1	15 ± 8	0.31 ± 0.01	9.1	1.22 ± 0.12
99	36 ± 15	1.1	25 ± 6	0.74	25 ± 39	0.34	18 ± 10			
107	12 ± 6	0.35	39 ± 21	1.1	21 ± 17	0.62	18 ± 8	0.23 ± 28	6.8	0.44 ± 0.07
114	12 ± 0	0.35	16 ± 4	0.47	13 ± 19	0.38	7 ± 5	<0.01	<0.3	0.06 ± 0.03
128	10 ± 4	0.29			27 ± 14	0.79	9 ± 8	0.06 ± 0.08	1.8	0.25 ± 0.27
156	2 ± 0.7	0.06			9 ± 21	0.27	2 ± 0.2	<0.01	<0.3	
					Zineb: First Treatment					
56	220 ± 287	5.2						0.26 ± 0.09	6.2	
56.3	83 ± 21	2.0						0.08 ± 0.02	1.9	
57	46 ± 28	1.1						0.30 ± 0.32	7.1	
60	99 ± 44	2.4						0.05 ± 0	1.2	
63	30 ± 4	0.80						0.06 ± 0.05	1.6	
67	26 ± 35	0.70						0.31 ± 0.11	8.4	
71	78 ± 29	2.2						0.55 ± 0.16	14.8	
72	31 ± 30	0.88						0.40 ± 0.17	9.7	
77	19 ± 4	0.49						0.34 ± 0.17	9.7	
85	16 ± 4	0.47						<0.01	<0.1	
					Zineb: Second Treatment					
86	50 ± 6	1.5	86 ± 31	2.5	51 ± 20	1.5	24 ± 8	0.03 ± 0.1	0.9	0.98 ± 0.34
87	24 ± 4	0.71	86 ± 19	2.5	88 ± 54	2.6	29 ± 17	0.25 ± 0.32	7.4	0.80 ± 0.73
89	32 ± 1	0.94	49 ± 18	1.4	57 ± 78	1.7	15 ± 6			4.6 ± 3.1
93	55 ± 29	1.6	72 ± 34	2.1	40 ± 47	1.2	16 ± 5			1.2 ± 0.30
98	22 ± 13	0.65	73 ± 0.6	2.1	45 ± 24	1.3	24 ± 0.2	0.41 ± 0.08	12.1	2.0 ± 0.74
99	26 ± 4	0.77	45 ± 1	1.3	21 ± 20	0.62	13 ± 3			
107	13 ± 5	0.38	28 ± 8	0.82	21 ± 7	0.62	14 ± 3	0.04 ± 0.04	1.2	0.28 ± 0
114	12 ± 0	0.35	29 ± 7	0.85	27 ± 18	0.79	4 ± 0.3	0.01	0.3	0.17 ± 0.08
128	13 ± 8	0.38			9 ± 4	0.27	4 ± 1	0.04 ± 0.02	1.2	0.12 ± 0.14
156	2 ± 0.1	0.06			5 ± 7	0.15	39 ± 25	<0.01	<0.03	

[a] By combustion. [b] Mean and standard deviation. [c] One replication missing.

fungicide applied, only 2.9% of the [^{14}C]maneb and 5.3% of the [^{14}C]zineb were trapped by the filters (Table VII). This discrepancy may be explained by the fact that in a separate test (Table VIII) the filters trapped only 50% of the volatized EBDC products off fiberglass cloth. The dissipation of the fungicides from the chamber walls then was probably because of low-molecular-weight volatile products, i.e., CS_2 not trapped by the filters, or if higher molecular compounds were trapped, they may have undergone degradation in the filters, also.

Composite of ^{14}C in Microagroecosystem Chamber. A composite of the total ^{14}C-labeled maneb and zineb introduced into the chamber and found in the various chamber components is given in Table VII. There were four major repositories for the ^{14}C: (1) plant leaves, (2) plant residue, (3) soil, (4) chamber walls, and possibly a fifth, the air. Under field conditions, chamber walls would be excluded. Thus, nearly all of the maneb and zineb (measured as ^{14}C) applied to tomatoes would eventually reach the soil or be dissipated into the air.

The amounts of maneb or zineb found on the tomato fruit was <0.3% of that applied. Since fruit production was probably less than that under field conditions, possibly as much as <0.5% of the fungicide may contaminate tomato fruit under field conditions. The amounts of ^{14}C from maneb and zineb in the leachate water were negligible.

Total recoveries of maneb and zineb from the microagroecosystem chambers show 67% of ^{14}C from maneb and 64% of ^{14}C from zineb was accounted for. These recoveries (maneb, 67%; zineb, 64%) resembled those recovered (maneb, 68%; zineb, 72%) obtained when the fungicides, in a separate test, were placed on fiberglass cloth and the trapping efficiency of the air filters tested (Table VIII). Presumably, about 30% of the fungicides were lost through volatilization of low-molecular-weight degradation products.

Table V. Concentration of Maneb and Zineb Measured as Ethylenediamine (EDA) and ETU in/on Soil in Microagroecosystem Chambers

		EDA			ETU	
			^{14}C			
day	soil depth, cm	GLC, ppm[a]	extracted, ppm	nonextracted, ppm	GLC, ppb	^{14}C, ppb
			Maneb			
86	slides[b]		10.09 mg/m²		106 μg/m²	235 μg/m²
88	0-1	0.23 ± 0.06	0.28 ± 0.004	0.054	30 ± 15	8
92	0-1	0.14 ± 0.04		0.062	ND	4
94	0-1	0.16 ± 0.06	0.29 ± 0.01	0.012	ND	27
94	1-2	0.02 ± 0.06	0.004 ± 0.005	0.008	ND	ND
102	0-2	0.06 ± 0	0.60 ± 0.30	0.231	ND	0.1
102	2-4	ND[c]	0.06 ± 0.03	0.018	ND	4
156	0-5	0.01 ± 0.02	0.41 ± 0.28	0.203	ND	
156	5-10	ND	0.03 ± 0.03	0.004	ND	
156	10-15	ND	0.02 ± 0.005	0.005	ND	
$c_{1/2}$, days		36[d]			3	
k		−0.02			−0.23	
r		−0.96			−0.61	
			Zineb			
86	slides[b]		5.55 mg/m²		220 μg/m²	344 μg/m²
88	0-1	0.37 ± 0.29	0.26 ± 0.08	0.046	25 ± 11	23
92	0-1	0.29 ± 0.17		0.037	ND	6
94	0-1	0.45 ± 0	0.55 ± 0.17	0.055	ND	ND
94	1-2	0.04 ± 0.33	0.01 ± 0.004	0.004	ND	0.9
102	0-2	0.08 ± 0.38	0.68 ± 0.17	0.150	ND	0.8
102	2-4	ND	0.05 ± 0.001	0.022	ND	
156	0-5	0.01 ± 0	0.27 ± 0.04	0.104	ND	
156	5-10	ND	0.06 ± 0.009	0.017	ND	
156	10-15	ND	0.04 ± 0.02	0.023	ND	
$c_{1/2}$, days		23			0.5	
k		−0.03			−1.30	
r		−0.95			−0.84	

[a] Mean and standard deviation of dry weight. [b] Measured from glass slides placed on the soil surface during treatment. [c] None detected. [d] Assumed to be in surface centimeter of soil.

Table VI. Concentration of Maneb and Zineb Measured as Ethylenediamine (EDA) and ETU in Leachate Water from Microagroecosystem Chambers

	fungicide							
	maneb				zineb			
	EDA		ETU		EDA		ETU	
day	GLC, μg/L	^{14}C, μg/L	GLC,[a] μg/L	^{14}C, μg/L	GLC, μg/L	^{14}C, μg/L	GLC,[a] μg/L	^{14}C, μg/L
71	0.063		ND		0.46		ND	
98	1.2	34	0.35 ± 0.26	0.26	0.45	40	0.34 ± 0.49	0.16

[a] Mean and standard deviation.

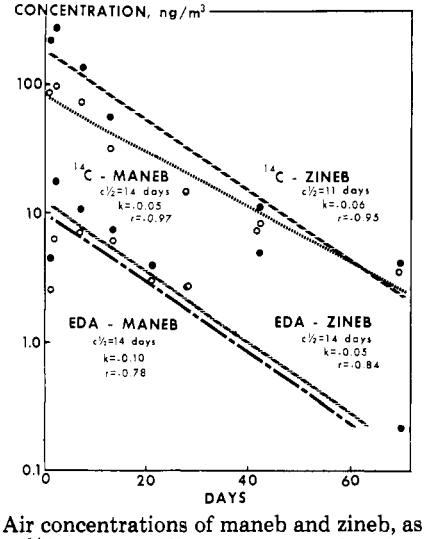

Figure 4. Air concentrations of maneb and zineb, as measured by EDA and ^{14}C when, applied to tomatoes in microecosystem chambers.

Table VII. Percentage Recovery of Maneb and Zineb from Microagroecosystem Chambers Based on ^{14}C Applied

experimental phase	maneb, %	zineb, %
plant leaves	12.7	17.3
plant residue[a]	15.5	8.14
tomatoes	0.1	0.3
soil[a]	14.4	15.6
leachate water	0.05	0.05
air	2.9	5.3
chamber walls	21.5	17.6
total	67.2	64.4

[a] Based on concentration at end of experiment.

Total ^{14}C recovered from maneb and zineb treatments in the microagroecosystem chambers were (Table VII) 99 and 90%, respectively, of that in the filter trapping efficiency tests (Table VIII).

Air Filter Trapping Efficiency. Table VIII gives the results from three tests for determining the efficiency of the air filters for trapping [^{14}C]maneb, [^{14}C]zineb, and [^{14}C]ETU. If it is assumed that, that which is not found on fiberglass cloth volatilizes either as the parent com-

Table VIII. Mean and Standard Deviation of Percentage Recovery for Trapping Efficiencies of Air Filters for ^{14}C-Labeled Maneb, Zineb, and ETU

medium	% recovery, test number 1	2	3	mean, %	filter trapping efficiency, %
		Maneb			
filters	27.6 ± 1.9	36.0 ± 2.4	27.5 ± 11.3	30.4 ± 11.7	48.9
fiberglass cloth	37.8 ± 2.0	37.9 ± 2.5	37.6 ± 9.3	37.8 ± 9.8	
total found	65.5 ± 3.5	74.0 ± 4.6	65.1 ± 22.9	68.2 ± 23.6	
		Zineb			
filters	30.4 ± 2.9	36.7 ± 1.1	42.2 ± 14.9	36.4 ± 15.2	56.4
fiberglass cloth	41.3 ± 3.0	38.7 ± 2.4	26.4 ± 3.4	35.5 ± 5.1	
total	71.7 ± 2.0	74.4 ± 1.7	68.6 ± 18.4	71.6 ± 18.6	
		ETU			
filters	30.5 ± 1.5	40.1 ± 0.7	38.7 ± 6.2	36.4 ± 6.4	63.1
fiberglass cloth	46.7 ± 1.1	46.6 ± 1.8	33.6 ± 8.4	42.3 ± 8.7	
total	77.2 ± 2.4	86.7 ± 2.0	72.3 ± 10.5	78.7 ± 11.0	

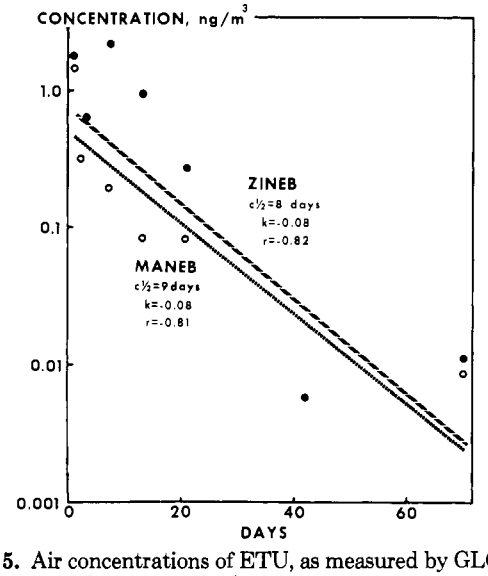

Figure 5. Air concentrations of ETU, as measured by GLC, when maneb and zineb were applied to tomatoes in microecosystem chambers.

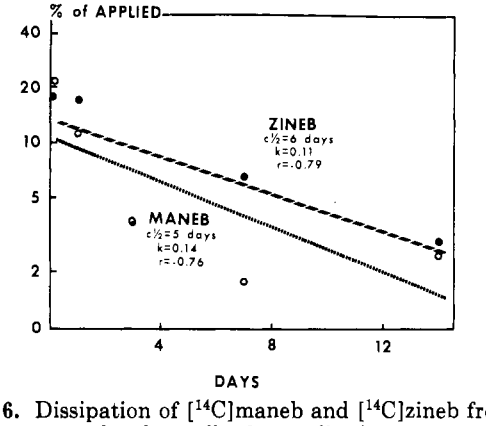

Figure 6. Dissipation of [^{14}C]maneb and [^{14}C]zineb from microagroecosystem chamber walls after application to tomato plants.

pound or as degradation products, then a filter trapping efficiency can be calculated. The polyurethane filters were capable of trapping only about 50% of the volatile products for maneb and zineb and about 60% for ETU.

CONCLUSIONS

Maneb and zineb degraded partially to ETU on tomato fruit with an apparent buildup for possibly 3 days after application. However with sprinkle irrigation, the ETU is dissipated rapidly and no longer detectable after 3 weeks even though maneb and zineb (measured as EDA) were detectable for 10 weeks. The $c_{1/2}$ value for ETU, after the initial buildup, was 3 days for maneb and 9 days for zineb.

The $c_{1/2}$ for both maneb and zineb on tomato leaves were 14 days. ETU was present (<0.5 ppm measured by GLC) on tomato leaves for about 30 days after application with little apparent loss, i.e., the rate of formation equaled the rate of loss.

Maneb and zineb (measured as EDA) do not move downward in soil with a result that little was found in the leachate water (<1.2 μg/L). However, soluble ^{14}C degradation products (<40 μg/L) of maneb and zineb (not measured as EDA or ETU) did move through the soil with the leachate water. ETU was not detected in soil beyond 2 days after application.

Maneb and zineb (measured as EDA) concentrations (<20 ng/m^3) in air had $c_{1/2}$ values of 7–14 days. However, [^{14}C]maneb and [^{14}C]zineb degradation volatile products were present in concentrations (<250 ng/m^3) several orders of magnitude greater than the EDA measured products. Presumably, these volatile products enhanced ^{14}C losses; hence only 65% of the applied ^{14}C was accounted for in the chambers. However, [^{14}C]maneb and [^{14}C]zineb $c_{1/2}$ values in air (11–14 days) were similar to the EDA measured values (7–14 days). ETU $c_{1/2}$ values in air for both fungicides were 8–9 days.

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Fate of Diflubenzuron in Water

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The fate of the insect growth regulator diflubenzuron (Dimilin, *N*-[[(4-chlorophenyl)amino]-carbonyl]-2,6-difluorobenzamide) was studied in distilled water and in acidic (pH 4.0) and alkaline (pH 10.0) buffers. Heat (121 °C) catalyzed degradation of diflubenzuron in these aqueous media at levels greatly above its solubility in water resulted in rapid degradation to as many as seven identified products: (4-chlorophenyl)urea, 2,6-difluorobenzoic acid, 2,6-difluorobenzamide, 4-chloroaniline, *N*,*N*′-bis(4-chlorophenyl)urea, a 2,4-quinazolinedione derivative that resulted from expulsion of HF from diflubenzuron with cyclization at the anilino nitrogen and the ortho carbon of the benzoyl ring, and a further reaction product of the quinazolinedione compound. Under less vigorous conditions (0.1 ppm of [^{14}C]diflubenzuron in water or buffer, 36 °C), the rate of degradation was highly dependent upon pH. At pH 10.0, the half-life of diflubenzuron was <3 days; but at pH 4.0, degradation was not detected even after 56 days. In distilled water (pH ~6.0), the half-life of diflubenzuron was about 7 days. The major degradation products were (4-chlorophenyl)urea and 2,6-difluorobenzoic acid, but small amounts of 2,6-difluorobenzamide and the quinazolinedione product were also formed. When tested as an ovicide against the boll weevil or as a mosquito larvicide against *Culex quinquefasciatus*, the quinazolinedione derivative did not exhibit appreciable diflubenzuron-like biological activity.

The insect growth regulator diflubenzuron (1, Dimilin, *N*-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide, Figure 1) is a highly efficacious insecticide that acts by inhibiting the synthesis of cuticle chitin, thus disrupting normal growth and development processes of developing insects (Hajjar and Casida, 1978; Mulder and Gijswijt, 1973; Post et al., 1974; Verloop and Ferrell, 1977). Diflubenzuron is particularly toxic to the larval stages of certain Lepidoptera (Granett and Dunbar, 1975; Tamaki and Turner, 1974) and mosquito larvae (Mulla et al., 1974; Schaefer et al., 1975). With several other insect species, including the boll weevil (*Anthonomous grandis* Boheman), house fly (*Musca domestica* L.), and stable fly (*Stomoxys calcitrans* L.), exposure of the adult insects to 1 causes them to lay eggs that fail to hatch (Moore and Taft, 1975; Grosscurt, 1976; Wright and Harris, 1976; Wright and Spates, 1976). This effect is apparently due to an ovicidal action and not sterility of the treated adults since the larvae appear to undergo more or less normal development within the eggs but are unable to hatch (Grosscurt, 1976; Verloop and Ferrell, 1977). Secretion of unmetabolized 1 into the eggs apparently accounts for the ovicidal effects observed (Ivie and Wright, 1978).

Since 1 has considerable potential as an insect control agent, the environmental fate of the compound should be thoroughly investigated. Several workers have already reported on the interactions of 1 with various components of the environment. The fate of 1 has been studied in several species of insects (Chang, 1978; Chang and Stokes, 1979; Still and Leopold, 1978; Ivie and Wright, 1978; Metcalf et al., 1975; Verloop and Ferrell, 1977) and mammals (Ivie, 1978; Metcalf et al., 1975). The persistence and fate of 1 in and on plants and in soils has also been reported (Bull and Ivie, 1978; Metcalf et al., 1975; Schaefer and Dupras, 1977; Verloop and Ferrell, 1977).

Although 1 has low water solubility (0.2–0.3 ppm; Ferrell, 1978), water may represent a significant route through which nontarget organisms can be exposed to 1 or its degradation products, particularly if 1 is used as a mosquito larvicide. However, only very limited data are available on the fate of 1 in water. Schaefer and Dupras (1976) reported that dilute solutions of 1 were not stable in field waters and that in tap waters stability was least when both pH and water temperature were relatively high. They obtained evidence that 1 in water degrades to (4-chlorophenyl)urea, but did not determine the possible occurrence of other degradation products.

The purpose of our investigation was to obtain more definitive information on the fate of 1 in water, particularly as influenced by pH. In some studies, large amounts of

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