

disk electrode has been used to determine the electron stoichiometry  $n$ . Information concerning the voltammetric properties and electron stoichiometry of nitrofen and knowledge of the redox behavior of other nitroaromatic compounds should permit us to propose a reasonable mechanism for the oxidation-reduction of nitrofen in protolytic and aprotic solvents.

**Registry No.** Acifluorfen, 50594-6-6; AFM, 50594-67-7; bifenox, 42576-02-3; nitrofen, 1836-75-5; nitrofluorfen, 42874-01-1; oxyfluorfen, 42874-03-3; MC-7783, 74434-43-8; MC-10982, 74315-61-0.

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## Distribution of Butylate, Heptachlor, Lindane, and Dieldrin Emulsifiable Concentrated and Butylate Microencapsulated Formulations in Microagroecosystem Chambers

Ralph G. Nash

The comparative distribution of butylate herbicide and heptachlor, lindane, and dieldrin insecticides as emulsifiable concentrated (EC) and butylate microencapsulated (ME) formulations in microagroecosystem chambers was determined. [ $^{14}\text{C}$ ]Butylate EC at 5.5 and ME at 5.2 and the insecticides at 2 kg ha $^{-1}$  were sprayed onto soil. One treatment set was immediately incorporated and a second set was incorporated 24 h later. Corn was planted, and soil, air, and corn samples were taken periodically for pesticide assay. For butylate ME and the insecticides, the distribution in percent of applied after 52 days in soil was 65-69% for immediate incorporation and 58-63% for delayed incorporation and in corn and weeds <1% for insecticides and 5% for butylate ( $^{14}\text{C}$  equiv). Loss by vaporization for heptachlor, lindane, and dieldrin, respectively, was 15, 12, and 3% from immediate incorporation and 38, 26, and 4% from delayed incorporation. Butylate EC ( $^{14}\text{C}$  equiv) immediate and delayed incorporation, respectively, resulted in 18 and 6% remaining in soil and 5 and 1% in corn and weeds.

A farm practice that is becoming more popular is that of minimum till, because erosion, energy, and costs usually are reduced. One aspect for successful minimum-till practices will, in many cases, involve use of chemical pesticides applied to soil surfaces rather than soil incorporation. Depending upon a pesticide's vapor pressure and formulation, considerable pesticide losses may occur. The body of information on vapor losses of pesticides with time under various soil and plant conditions is small and limited to a few pesticides, primarily chlorinated hydrocarbon insecticides.

S-Ethyl diisobutylthiocarbamate (butylate) is a preemergent herbicide used to control grasses and some broadleaf weeds. Because butylate has a high vapor pressure (1735 mPa or  $13 \times 10^{-3}$  mmHg at 25 °C) (Mullison et al., 1979)

and consequent high losses through volatilization, it must be incorporated into the soil in <1 h after application according to labeled instructions. An alternative has been the development of microencapsulation to reduce butylate losses through volatilization.

Atallah et al. (1979) in a comparative volatilization study of liquid (EC) and granular (G) formulations of 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindan (chlordane) and 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (heptachlor) mixed in laboratory soil found chlordane EC formulations were 20 times more volatile than the corresponding G formulation. Heptachlor EC formulations was 5-10 times more volatile than the G formulation.

This paper compares the distribution of microencapsulated (ME) butylate with emulsifiable concentrated (EC) butylate, heptachlor, the  $\gamma$ -isomer of 1,2,3,4,5,6-hexachlorocyclohexane (lindane), and 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,exo-5,8-dimethanonaphthalene (dieldrin) formulations in microagroecosystem chambers.

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## MATERIALS AND METHODS

**Experimental Conditions.** Butylate ( $[1-^{14}\text{C}]$ isobutyl with a specific activity of  $0.1 \mu\text{Ci g}^{-1}$ ) EC formulation (85.1%) at  $5.5 \text{ kg ha}^{-1}$  a.i. and ME at  $5.2 \text{ kg ha}^{-1}$  and heptachlor, lindane, and dieldrin EC at  $2 \text{ kg ha}^{-1}$  were applied by spraying aqueous suspensions onto soil in microagroecosystem chambers. The microagroecosystems are large glass chambers 150 cm long, 50 cm wide, and 100 cm above 15 cm of soil (Beall et al., 1976; Nash et al., 1977). The soil was a Galestown (Psammentic Hapludults) sandy loam (pH value = 6.7, organic matter = 5.2%, and 33-kPa moisture tension = 15.6%).

Both butylate formulations were applied to two chambers, and the insecticides were applied to four chambers in a combined 40-mL aqueous suspension containing an emulsifier. Immediately after application, the pesticides in one chamber each receiving butylate EC or ME formulations and two chambers receiving the insecticides were incorporated into the soil. Pesticide incorporation in the remaining two chambers was delayed 24 h. Incorporation was by first turning the soil over to a depth of 5–7 cm with a garden spatula and then mixing with a small one-hand garden rake. One chamber was not treated with pesticide, but received the pesticide carrier as delayed incorporation. Subsequently, *Zea mays* L. (corn) Southern States Hybrid No. 875 was planted, and the soils were automatically maintained moist near the 33-kPa tension. (Soil moisture tensiometers were set to start irrigation at 40 kPa.) The experiment was conducted over a 52-day period from May 5 to June 26, 1981, using ambient greenhouse light. Hence, soil temperatures gradually rose from a daily mean of 20 to 28 °C. On May 22,  $1000 \text{ kg ha}^{-1}$  of 5–10–5 NPK fertilizer was broadcast onto the soil.

**Sampling.** Soil (twice on day 0 and once on days 1 and 2) and air (4 times on day 0, twice on day 1, and once on day 2) samples were taken initially and then twice weekly thereafter. Corn (a portion of uppermost leaf) samples were taken weekly initially and twice weekly thereafter, beginning the 24th day. Soil samples consisted of seven (2 cm in diameter) cores taken the full depth of the soil. Each core hole was filled immediately (by using a powder funnel) with about 10 cm of nontreated plus 5 cm of treated soil, except during day 0 for the chambers with delayed pesticide incorporation. Air sampling was by filtering the air exhausted from the chambers with suction fans. The exhausted chamber air was filtered through polyurethane foam (Beall et al., 1976), which trapped most of the chlorinated hydrocarbon insecticides and some of the butylate (Nash, 1984). No butylate volatilization is reported, because of the inefficient trapping of butylate vapors. The chamber contains 12 air filters, but only four filters (one at 20, 40, 60, or 80 cm above the soil) were collected for assay (Nash, 1983). At experimental termination, corn and weed weights were determined and subsamples of a 5-cm section above the first internode of the corn stalk, corn leaves, and weeds were harvested. Pesticide concentration in corn at termination was based on a mean of the corn stalk and leaves concentration.

**Analytical.** The soil and corn samples and air filters were extracted by steam distillation (Nash, 1984). Prior to steam distillation, the soil or plant samples were placed in a boiling flask and the air filters in the neck of the flask. The pesticide is driven from the sample with boiling water or steam, and both the steam and pesticide are trapped by condensing. Subsequently, the distillate was extracted with  $\text{CCl}_4$ . The  $\text{CCl}_4$  extract was split three ways. Two subextracts were taken just to dryness and redissolved in 2,2,4-trimethylpentane or liquid scintillation solution. The

Table I.  $[^{14}\text{C}]$ Butylate Equivalent Residues Remaining in Soil after Steam Distillation-Extraction

day	formulation, ppm of butylate equiv <sup>a</sup>	
	emulsifiable concentrated	micro-encapsulated
0.39	0.004	1.08
0.60	0.019	1.02
1.63	0.045	0.55
3.62	0.012	1.01
6.41	0.067	0.99
11.33	0.050	0.79
14.33	0.073	0.68
17.61	0.045	1.00
21.55	0.048	0.91
24.34	0.055	0.85
27.63	0.071	0.72
30.60	0.063	0.52
34.43	0.101	1.02
38.41	0.064	0.94
41.64	0.081	1.10
45.46	0.105	0.62
48.60	0.138	1.38
52.58	0.072	0.67

<sup>a</sup> Calculated initial butylate was 4.3 and 3.8 ppm for EC and ME formulations, respectively. Initial measured butylate was  $3.5 \pm 1.1$  and  $4.0 \pm 1.1$  ppm for EC and ME, respectively, based on the first two samplings.

2,2,4-trimethylpentane was assayed for insecticides by gas-liquid chromatography (GLC) using an electron-capture detector. The second subextract was assayed for  $^{14}\text{C}$  by liquid scintillation counting. The remaining  $\text{CCl}_4$  extract was assayed for butylate by GLC by using a photoionization detector.

Air samples were corrected for air filter trapping efficiency, and all samples were corrected for analytical recovery efficiencies. Both the extracted soil and plant samples were oxidized to assay for steam nonextractable  $^{14}\text{C}$  residues.

## RESULTS AND DISCUSSION

**Comparative Pesticide Persistence.** Pesticide persistence in soil is shown in Figure 1. The dissipation of heptachlor, lindane, and dieldrin in soil was fairly uniform with half-concentration ( $C_{1/2}$ ) values of 120, 120, and 116 days, respectively. Dissipation of these insecticides, especially dieldrin, incorporated in soil usually is much slower with  $C_{1/2}$  values of >1 year (Nash and Woolson, 1967, 1968). When compared to dissipation from a soil surface, heptachlor, lindane, and dieldrin  $C_{1/2}$  values were 2.5, 4.3, and 19 days, respectively (Nash, 1983).

Butylate dissipated more rapidly with  $C_{1/2}$  values of 25 and 80 days for the EC and ME formulations, respectively (Figure 1). After day 0, delayed incorporation only reduced the amount dissipated; it did not increase or decrease the rate of dissipation when compared to immediate incorporation.

Heptachlor epoxide soil concentration increased with time. The amounts of heptachlor epoxide compared to heptachlor remained low.

In a previous experiment, butylate EC formulation recovery from soil, corn, and air filters was nearly 100% from fortified samples (Nash, 1984). Butylate ME formulation recovery was only 35%, which reflected the inability of the steam distillation method to extract butylate from microencapsulated material.

Butylate or butylate metabolite extraction from soil samples in this study was incomplete (Table I). The  $[^{14}\text{C}]$ butylate equivalent residues in soil from the EC formulation probably represents butylate metabolic and

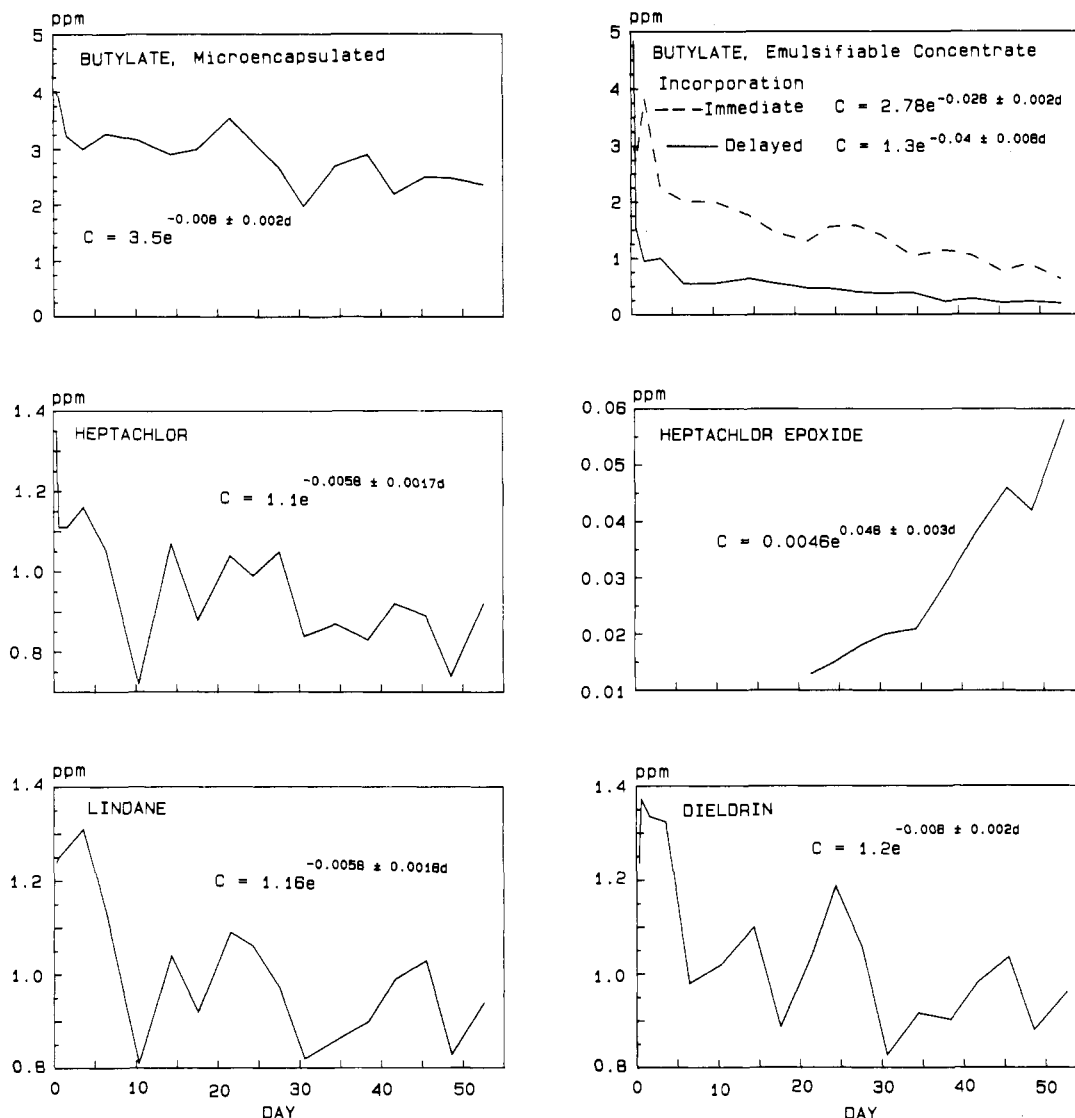


Figure 1. Dissipation of pesticides from Galestown sandy loam soil. Curves represent both immediate and delayed (24 h) incorporation, except for butylate EC. All equations have a 99% confidence level.

Table II. First-Order Equations ( $r = 99\%$ ) for Pesticide Volatilization (Flux =  $\text{g ha}^{-1} \text{ day}^{-1}$ ) from Emulsifiable Concentrate Formulation Applied to Soil

pesticide	day			$F_{1/2}$ , days <sup>b</sup>
	0	0-3 <sup>a</sup>	1-52 <sup>a</sup>	
	Immediate Incorporation			
heptachlor	$F = 900e^{-2.4d}$	$F = 330e^{-0.90d}$	$F = 36.6e^{-0.088d}$	8
lindane	$F = 330e^{-2.4d}$	$F = 110e^{-0.79d}$	$F = 10e^{-0.042d}$	16
dieldrin	$F = 36.6e^{-2.2d}$	$F = 12.2e^{-0.64d}$	$F = 7.4e^{-0.037d}$	19
heptachlor epoxide			$F = 0.01e^{0.044d}$	
	Delayed Incorporation			
heptachlor	$F = 2980e^{-1.8d}$			
lindane	$F = 1480e^{-1.4d}$			
dieldrin	$F = 180e^{-1.3d}$			

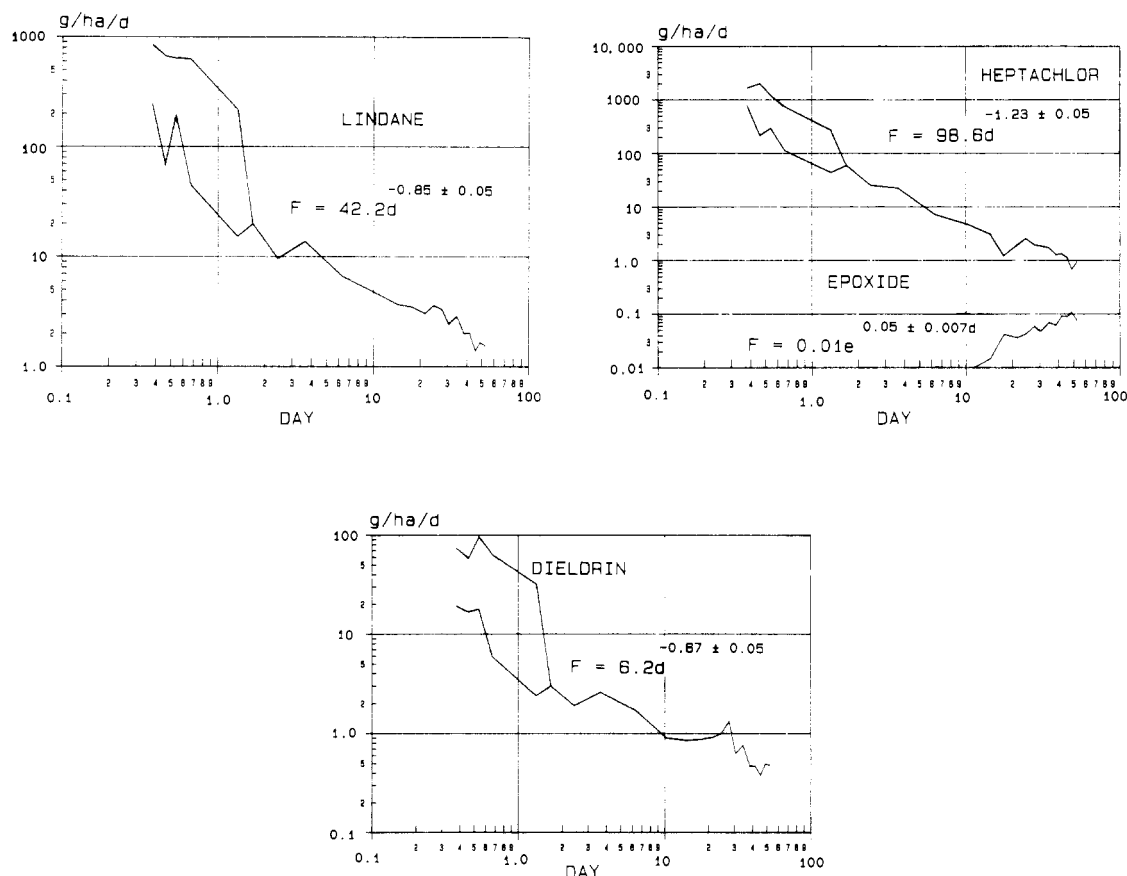
<sup>a</sup> Includes both immediate and delayed incorporation. <sup>b</sup> Time for flux amount to decline by half, based on 1-52-day period.

degradation products. Initially, nearly all [<sup>14</sup>C]butylate EC was extracted from soil, but with time greater amounts of <sup>14</sup>C were not extracted. The maximum value of 0.14 ppm represents only 3% of the application. The nonextractable EC <sup>14</sup>C residues in soil can be described by  $C = 0.015d^{0.47 \pm 0.08}$  ( $r^2 = 0.71$  with 99% confidence) ( $C = \text{ppm}$  and  $d = \text{day}$ ), which presumably indicates the rate of residue binding.

Nonextractable soil residues from the ME formulation represent mostly the [<sup>14</sup>C]butylate remaining in the mi-

croencapsulation and possibly with time some <sup>14</sup>C nonextractable butylate residues. There was no statistically significant increase or decrease in nonextractable soil <sup>14</sup>C ME residues over the course of the experiment.

**Comparative Pesticide Volatilization.** Immediate incorporation of the pesticides reduced volatilization considerably compared to the delayed incorporation (Tables II and III and Figure 2). The delayed incorporation resulted in losses of  $\approx 2\%$  of the application for dieldrin,  $\approx 15\%$  for heptachlor and lindane, and nearly 65% for



**Figure 2.** Volatilization (flux) of insecticides from immediate (lower) or delayed (upper) (24 h) incorporation into Galestown sandy loam soil. Equations are for incorporated insecticides and have a 99% confidence level.

**Table III.** Comparative Flux ( $\text{g ha}^{-1} \text{ day}^{-1}$ ) for Insecticides on Day 0

pesticide	vapor pressure, <sup>a</sup> mPa, at 30 °C	immediate incorporation	delayed incorporation	ratio of delayed incorporation/ immediate incorporation
heptachlor	40	110	520	4.7
lindane	17	47	360	7.6
dieldrin	1.3	5.7	45	7.9

<sup>a</sup> Bowery (1964), Spencer and Cliath (1976), and Spencer and Cliath (1976), respectively.

butylate EC (Figure 1). Compared to immediate incorporation, delayed incorporation of butylate ME resulted in almost no observable losses; hence, the ME results for immediate and delayed incorporation were combined (Figure 1). When these data are compared to volatilization from soil or plant surfaces (Nash, 1983; Taylor et al., 1977), the importance of immediate incorporation to reduce volatilization is readily apparent.

The decline in pesticide flux was not strictly pseudo first order over the course of the experiment. There appeared to be at least two, if not three, distinct first-order declining periods (Table II). Previous results have shown this also (Nash and Beall, 1980; Nash et al., 1977; Taylor et al., 1977). Therefore, a power function equation was developed, which appears to give a good description of the flux over the entire course of the experiment, except during the initial period (Figure 2).

Comparative fluxes on day 0 for the incorporated and

delayed incorporated insecticides are given in Table III. Delayed incorporation resulted in 5–8 times more volatilization. Volatilization depended on the insecticide vapor pressure.

Flux rate of decline of  $-2.4$  (exponent or first-order slope) on day 0 for immediate incorporation of insecticides was nearly the same but less uniform (about  $-1.5$ ) than for the delayed incorporation (Table II). The same phenomenon was observed previously (Nash, 1983). Apparently, there was a rather uninhibited flux decline during day 0. The flux amounts for the insecticides reflected their partial pressures. However, as the insecticides on the soil surface were depleted, factors such as diffusion and adsorption limited volatilization of pesticides from below the soil surface. With time, surface soil depletion of the more volatile pesticides reduced the amount available for volatilization compared to the less volatile pesticides. After day 0, the rate of volatile pesticide decline in air continued to decrease rapidly, because of pesticide depletion, whereas the rate of nonvolatile pesticide decline in air was less rapid because the soil depletion rate was slower. All of these factors give the impression of a series of first-order rate amount declines of pesticide in air, which can best be described with a power function equation (Figure 2).

The conversion of heptachlor to its epoxide in the environment is well-known (Lichtenstein and Schulz, 1960). Volatilization of heptachlor epoxide increased throughout the course of the experiment. Eventually, the amount volatilized would peak and then decline as the amount of heptachlor remaining to be oxidized decreased. Heptachlor epoxide in air was measurable after day 6 (Figure 2) but was not found in soil until after day 21 (Figure 1).

**Pesticides in/on Plants.** Pesticides in/on plants are given in Tables IV and V. The experiment did not establish whether the pesticides were in or on the plants or

Table IV. Insecticides in/on Plants<sup>a</sup>

day	plant	compound, ppb fresh weight			
		heptachlor	heptachlor epoxide	lindane	dieldrin
24.5	corn leaf	170 ± 110	330 ± 170	760 ± 300	250 ± 80
30.6	corn leaf	140 ± 70	70 ± 20	510 ± 160	60 ± 20
38.4	corn leaf	70 ± 30	50 ± 30	140 ± 70	50 ± 20
41.7	corn leaf	90 ± 60	40 ± 30	130 ± 90	50 ± 40
45.4	corn leaf	30 ± 10	30 ± 10	50 ± 30	ND <sup>b</sup>
52.3	corn leaf	20 ± 10	30 ± 20	50 ± 30	ND
52.3	corn stalk	10 ± 0	180 ± 20	760 ± 100	400 ± 100
52.3	weeds	150 ± 60	70 ± 20	520 ± 15	410 ± 150

<sup>a</sup> From both immediate and delayed incorporation. <sup>b</sup> None detected.

Table V. <sup>14</sup>C Residues (ppm of Butylate Equivalent) in/on Plants

day	plant	formulation <sup>a</sup>							
		emulsifiable concentrated				microencapsulated			
		immediate incorporation		delayed incorporation		immediate incorporation		delayed incorporation	
		extractable	nonextractable	extractable	nonextractable	extractable	nonextractable	extractable	nonextractable
24.5	corn leaf	0.40	6.3	0.11	2.0	0.43	4.3	0.19	2.8
30.6	corn leaf	2.02	6.5	0.17	1.3	3.02	2.4	0.66	1.6
38.4	corn leaf	0.31	4.2	0.01	0.7	0.45	2.3	0.37	1.7
47.7	corn leaf	0.16	3.4	ND <sup>b</sup>	0.6	0.23	2.0	0.10	1.3
45.4	corn leaf	0.07	3.5	ND	0.8	0.05	2.3	0.04	1.3
52.3	corn leaf	0.01	3.2	ND	0.6	0.07	2.8	0.17	2.7
52.3	corn stalk	1.89	5.7	0.24	1.4	3.05	6.4	3.56	4.8
52.3	weeds	0.39	6.9	0.02	1.1	1.20	6.1	1.65	6.2

<sup>a</sup> A paired *t* test indicated no statistical differences between the two formulations. *t* tests indicated statistically higher differences for nonextractable compared to extractable <sup>14</sup>C residues (99%), immediate compared to delayed incorporation (EC = 99%, ME = 95%), and delayed ME compared to delayed EC (95%). <sup>b</sup> None detected.

whether the residues were the results of root uptake or leaf sorption of pesticide vapors. Previously, we (Beall and Nash, 1971) had established that about 1/3 of the heptachlor residues sorbed on soybean leaves were the result of sorption of heptachlor vapors and about 1/2 of dieldrin residues were the result of vapor sorption; the rest was by root uptake. Therefore, it must be assumed that some of the residues in/on both the corn and weeds were from vapor sorption.

The corn stalk contained some of the higher amounts for all the pesticides, except heptachlor, which would indicate root uptake was a major pathway for residues in corn grown in microagroecosystem chambers. Root uptake was probably the major pathway for heptachlor, also, but some of the heptachlor was oxidized to its epoxide with the epoxide being more readily translocated [Table IV (Beall and Nash, 1971)]. Leaf residues decreased with time for several reasons. The rapid growth of the corn would dilute the residues present unless sorption was maintained proportionately. The upper leaf was always sampled, which would increase length of translocation from the roots. The upper leaf would become more shielded from vapors as the plant grew. Previous results have demonstrated that upper plant parts were less contaminated with dieldrin, heptachlor, and heptachlor epoxide than lower plant parts whether from root uptake or vapor sorption (Beall and Nash, 1971).

Lindane has been shown to be taken up readily by many crops in greater amounts than either heptachlor or dieldrin (Morrison et al., 1948; Nash, 1974; Nash and Harris, 1973).

No identifiable (by GLC) butylate was extracted from the corn by steam distillation. However, considerable nonextractable <sup>14</sup>C residues were found in the upper corn leaves, corn stalk, and weeds from both formulations (Table V). In all cases, except day 30.6, immediately incorporated microencapsulated, extractable residues were

less than the nonextractable butylate residues and with time became proportionately less than the nonextractable residues.

Total [<sup>14</sup>C]butylate residues in corn were similar for both formulations (Table V). A paired *t* test indicated no statistically significant differences between the two formulations. However, both immediately incorporated formulations resulted in statistically higher [<sup>14</sup>C]residues than the delayed incorporation. There is a rational explanation for the higher EC immediately incorporated residues in corn, because of the higher [<sup>14</sup>C]butylate amounts in soil from the immediately incorporated EC compared to delayed incorporation (Figure 1), but there does not seem to be an explanation of why 1 day's delay of incorporation of the ME formulation would result in lesser <sup>14</sup>C residues in corn. The corn was not even planted until day 1, immediately after the ME was incorporated. Concentrations of butylate ME in soil were the same for both immediate and delayed incorporation after day 1 (Figure 1) and should have been the same in the corn. ME <sup>14</sup>C residues in plant tissue were statistically higher than EC residues from the delayed incorporation.

The small amounts of insecticide sorbed by corn and weeds, either through root uptake or leaf sorption of vaporous insecticide, were not unlike those previously reported (Beall and Nash, 1971, 1972; Nash et al., 1970). The higher butylate plant sorption amounts presumably reflect butylate's (and probably butylate metabolites') greater water solubility [45 μg g<sup>-1</sup> (Mullison et al., 1979)] and resultant root uptake compared to those of the insecticides [water solubility of <7 μg g<sup>-1</sup> (Lichtenstein and Schulz, 1970)] rather than sorption of butylate vapors. If vaporous butylate was the major sorption route, butylate per se should have been found but was not. Because the [<sup>14</sup>C]-butylate residues were nonextractable, the implication would indicate root uptake with considerable metabolism

Table VI. Balance Sheet at End of 52 Days

component	pesticide, % of application				
	butylate		heptachlor <sup>a</sup>	lindane	dieldrin
	extractable	<sup>14</sup> C nonextractable			
	Immediately Incorporated Emulsifiable Concentrate				
soil (AR) <sup>b</sup>	15.7 ± 0.7	2.6 ± 1.8	68.6 ± 13.8	65.2 ± 13.9	66.5 ± 16.3
soil (IS) <sup>c</sup>	18.2 ± 3.2	3.0	83.6 ± 66.7	80.8 ± 66.3	77.2 ± 77.3
corn and weeds	0.009	5.1	0.2 ± 0	0.8 ± 0.2	0.4 ± 0.1
air			14.9 ± 2.3	11.7 ± 3.1	2.6 ± 0.9
total (AR)		23	84 ± 14	78 ± 14	70 ± 16
total (IS)		26	99 ± 67	93 ± 66	80 ± 77
	Delayed Incorporated Emulsifiable Concentrate				
soil (AR)	4.7 ± 0.8	1.08 ± 0.37	61.0 ± 35.2	57.7 ± 21.2	58.8 ± 22.1
soil (IS)	55.0 ± 3.2	1.3	74.4 ± 74.1	71.5 ± 68.3	68.2 ± 78.7
corn and weeds	0.0009	1.1	0.2 ± 0	0.7 ± 0.1	0.4 ± 0
air			38.0 ± 0	25.9 ± 3.7	4.4 ± 0.5
total (AR)		7	99 ± 35	84 ± 2	64 ± 23
total (IS)		57	113 ± 74	98 ± 68	73 ± 79
	Immediately Incorporated Microencapsulated				
soil (AR)	49.8 ± 6.5	19.1 ± 11.1			
soil (IS)	47.4 ± 7.4	18.2			
corn and weeds	0.013	5.3			
air					
total (AR)		74			
total (IS)		71			
	Delayed Incorporated Microencapsulated				
soil (AR)	49.2 ± 0.1	13.8 ± 3.5			
soil (IS)	46.9 ± 3.5	13.2			
corn and weeds	0.019	4.9			
air					
total (AR)		68			
total (IS)		65			
mean total (AR)	EC = 15	ME = 71	92	81	67
mean total (IS)	EC = 42	ME = 68	106	96	77

<sup>a</sup> Includes heptachlor epoxide as heptachlor equivalent. <sup>b</sup> AR = based on application rate. <sup>c</sup> IS = initial sampling.

of the butylate.

**Pesticide Balance Sheet.** The distribution of the pesticides among the environmental components at the end of the 52-day experimental period is given in Table VI. For butylate ME and heptachlor, lindane, and dieldrin, the distribution in "percent of applied" was 65–69% in soil for immediate incorporation and 58–63% for delayed incorporation and <1% in corn and weeds for the insecticides and 5% for butylate (<sup>14</sup>C equivalent). Loss to air by vaporization for heptachlor, lindane, and dieldrin, respectively, was 15, 12, and 3% from immediate incorporation and 38, 26, and 4% from delayed incorporation. Approximately 30% butylate ME was not accounted for. Butylate EC, immediate and delayed incorporation, respectively, resulted in 18 and 6% remaining in soil and 5 and 1% in corn and weeds and the remainder being lost primarily by vaporization with possibly some soil and plant decomposition to <sup>14</sup>CO<sub>2</sub>. Cliath et al. (1980) observed that 74% of EPTC, a related but more volatile thiocarbamate herbicide, was volatilized from irrigation water during a 52-h period.

Most of the heptachlor and lindane applied could be accounted for after 52 days (Table VI). Only about 80% of the dieldrin and butylate ME were found. For butylate ME and the insecticides, nearly 55–70% of the application rate remained in the soil at experimental termination. However, if the amount remaining in soil was based on the initial sampling, then nearly 70–80% remained in the soil. Therefore, about 10% of the insecticides and possibly butylate ME were lost during application or the first hour after application, when the first soil samples were taken.

**Weed Control.** Weed control determination was not an objective of the experiment. However, at the end of the experiment, weed weights were as follows: for control,

510; for delayed EC, 515; for delayed ME, 465; for incorporated ME, 395; for incorporated EC, 155 g. The incorporated EC gave the best weed control based on weed weight. Observations during the early weeks of the experiment indicated that both incorporated and delayed ME gave better weed control than either EC treatments.

The predominant weed species was *Chenopodium album* L. (common lambsquarters). Although there were fewer lambsquarters plants in the ME treated chambers, once established, they grew more vigorously, resulting in greater weed weight at the end of the experiment compared to that for the incorporated EC. The lesser weed weight for incorporated EC would result in the weeds extracting the least plant nutrients and hence would be the superior weed control method in this experiment.

There were no differences in final corn weight (≈2 kg) among any of the treatments.

#### SUMMARY AND CONCLUSION

The comparative distribution of heptachlor, lindane, dieldrin, and butylate ME resulted in >65% remaining in the soil from immediate incorporation and >58% from a 24-h period incorporation after 52 days. Vapor losses were 15, 12, and 3% for heptachlor, lindane, and dieldrin, respectively, from immediate incorporation and 38, 26, and 4% from delayed incorporation. Approximately 30% butylate ME was not accounted for, presumably because of both volatilization and degradation. About 65% of butylate EC was lost during the 24 h of delayed incorporation. Five percent of the butylate and <1% of the insecticides were found in the corn and weeds. Flux rate of decline was not strictly first order but a series of first order, which could be described by a power-function equation. After pesticide incorporation, the flux rates of decline and

soil dissipation rates were the same for both immediate and delayed incorporation.

Application of pesticides under minimum-till practices may result in considerable pesticide loss (4-65% depending upon their vapor pressure) through volatilization unless the pesticide is protected by formulation or incorporation.

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**Registry No.** Butylate, 2008-41-5; heptachlor, 76-44-8; lindane, 58-89-9; dieldrin, 60-57-1.

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## Diphenyl Ether Herbicides and Related Compounds: Structure-Activity Relationships as Bacterial Mutagens

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Several 4-nitrodiphenyl ether herbicides and related compounds or their nitroso, hydroxyamino, or amino derivatives are mutagens or promutagens in the *Salmonella typhimurium* (strain TA100)/microsome (S9) assay. Six of eleven 4-nitrodiphenyl ethers examined with no 3-substituent are direct-acting mutagens (4-9 revertants/nmol) and ten of eleven of the analogous 4-aminodiphenyl ethers (including those of the herbicides fluorodifen, nitrofen, and CNP) are mutagens (1-30 revertants/nmol) but only on metabolic activation (+S9). Herbicides with a 3-substituent (i.e., acifluorfen, acifluorfen-methyl, bifenoxy, bifenoxy free acid, chlomethoxynil, and oxyfluorfen) and their amino derivatives are generally not detected as mutagens (±S9). However, nitroso- and (hydroxyamino)nitrofen, nitroso-CNP, nitrosooxyfluorfen, and nitrosoacifluorfen are direct-acting mutagens (2-7 revertants/nmol). Rats reduce orally administered nitrofen, CNP, oxyfluorfen, acifluorfen, acifluorfen-methyl, and bifenoxy, presumably via nitroso and hydroxyamino intermediates, to the amino compounds that are excreted in the feces.

The herbicide nitrofen (Figure 1) is a teratogen (Gray et al., 1982) and carcinogen (Milman et al., 1978). It is also a promutagen in the *Salmonella typhimurium* assay, undergoing photochemical and metabolic activation to the nitroso and hydroxylamino derivatives (Draper and Casida, 1983). Aminonitrofen is both a promutagen and potent bactericide to *S. typhimurium* (Draper and Casida, 1983). This amino derivative also is an intermediary metabolite of nitrofen in rats (Costlow and Manson, 1983). These observations suggest that nitro reduction may play a role

in some of the adverse toxicological properties of nitrofen. The relevance of these findings to related 4-nitrodiphenyl ethers, including other commercial herbicides, is not known.

This study examines the structure-activity relationships for bacterial mutagenesis and toxicity of nitrodiphenyl ethers and their nitroso, hydroxyamino, and amino derivatives tested in the *S. typhimurium* assay with and without metabolic activation. It also considers the metabolism in rats of selected nitrodiphenyl ether herbicides to evaluate the possible presence of the nitroso, hydroxyamino, and amino derivatives as metabolites in mammals.

#### MATERIALS AND METHODS

**Spectroscopy.** Chemical ionization mass spectra (CI-MS) (70 eV, 0.8 torr of methane, solid probe) were recorded with a Finnigan Model 3200 instrument interfaced to a System Industries 150 data system. Proton nuclear

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