

waters. These results indicate that the rates of methoxychlor photolysis in pure water can be viewed only as minimum values for its rate of light-induced decomposition in natural waters.

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Factors Affecting the Stability of Dimilin in Water and the Persistence of Dimilin in Field Waters

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Dimilin (1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea), a very promising new mosquito control agent, persists in water long enough to accomplish mosquito control but does not have long-term stability in water. Persistence of this compound in water appears to be limited due to hydrolysis and to adsorption onto organic matter. It is least stable when water temperature and pH are both relatively high. Its persistence is not greatly affected by sunlight or by microorganisms. Application of a 25% wettable powder formulation disperses the active ingredient throughout water, but application of technical material in ethanol or of a 2.07 lb of active ingredient/gal of flowable liquid formulation causes a much greater concentration in the upper water levels for up to 3 days.

Dimilin (1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea) is a potent inhibitor of chitin synthesis in immature stages of insects (Post and Vincent, 1973) that has high biological activity against mosquitoes (Jakob, 1973; Schaefer et al.,

1974; Hsieh and Steelman, 1974; Mulla et al., 1975). An extensive, operational evaluation of Dimilin demonstrated its commercial potential as a mosquito larvicide (Schaefer et al., 1975); although some nontarget organisms were reduced by these treatments, their populations recovered within a short period of time (Miura and Takahashi, 1975).

Since Dimilin is projected to be used as a commercial larvicide, determination of factors affecting its stability

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Table I. Summary of Dimilin Field Tests, 1975

Field test no.	Date (1975)	MAD ^a	Location + habitat	Acres treated	Method of application	Formulation	Rate (lb of AI/acre)
75-1	5/15	Turlock	Colosso, pasture	40	Aircraft	25% WP ^b	0.02
75-3	5/29	Lake County	Boron Lake (pH 9.5)	6 ^c	Power sprayer	25% WP	0.1
75-4	6/12	Tulare	Monteiro, pasture	30	Aircraft	25% WP	0.04
75-5	6/17	Turlock	Colosso, pasture	40	Aircraft	25% WP	0.02
75-6	6/20	Tulare	Monteiro, pasture	30	Aircraft	25% WP	0.04
75-9	7/1	Tulare	Monteiro, pasture	30	Aircraft	25% WP	0.04
75-13	7/16	Turlock	Colosso, pasture	40	Aircraft	25% WP	0.02
75-14	7/17	Tulare	Monteiro, pasture	30	Aircraft	25% WP	0.04
75-23	8/13	Tulare	Machado, dairy drain	0.35	Power sprayer	FL ^d	0.1
75-25	8/19	Turlock	Colosso, pasture	40	Aircraft	25% WP	0.02
75-26	8/19	Kings	DeBrum, dairy drain	0.27	Hand sprayer	FL	0.1
75-28	8/27	Tulare	Machado, dairy drain	0.35	Power sprayer	FL	0.11
75-30	9/1	Consolidated	Roberts, pasture	6.5	Aircraft	1.0% G ^e	0.032
75-31	9/6	Consolidated	Lone Oak Rd., pasture	10	Aircraft	0.5% G	0.0227

^a Mosquito abatement districts. ^b 25% wettable powder. ^c Shoreline. ^d Flowable liquid (2.07 lb/gal). ^e Granules.

Table II. Recovery of Dimilin from Different Types of Water

Type of water	Concn, ppm		
	0.10	0.05	0.01
Tap	0.10	0.051	0.010
	0.098	0.050	0.0092
Pasture	0.099 ^a	0.051	0.0097
	0.10	0.052	0.010
Pond	0.10	0.052	0.0099
	0.099 ^a	0.052	0.010
Dairy drain	0.094	0.050	0.0093
	0.099	0.049	0.011
Sewage	0.097 ^a	0.049	0.010
	0.075	0.040	0.0067
	0.071	0.036	0.0073
	0.082	0.032	0.0032
	0.076	0.038	0.0030
	0.076 ^a	0.037	0.0050
	0.082	0.040	0.0073
	0.086	0.042	0.0069
	0.084 ^a	0.041	0.0071

^a Averages.

in water is very important. During 1975 the effects of temperature, pH, microbial decomposition, and sunlight on the stability of Dimilin were determined in laboratory and small-scale outdoor tests. Also, the concentration of Dimilin in the waters of large-scale field tests, in various types of natural mosquito breeding habitats, was measured.

MATERIALS AND METHODS

High-Performance Liquid Chromatography (HPLC). A Varian Model 8500 HPLC having a uv photometer (254 nm) was utilized for all quantitative analyses. A MicroPak-CH column (octadecylsilane bonded on 10 μ m particles), 2 mm \times 25 cm, provided reverse-phase separations using 60% methanol-40% water as the mobile phase, at a flow rate of 60 ml/h. At an ambient tem-

Table III. Effects of Temperature and pH on the Stability of Dimilin in Tap Water

pH	Held at $^{\circ}$ C	h after treatment				
		24	48	72	144	216
7.7	10	0.11 ^a	0.10	0.090	0.080	0.084
		0.088	0.097	0.093	0.081	0.085
10.0	10	0.096 ^b	0.10	0.092	0.081	0.085
		0.11	0.093	0.099	0.074	0.079
7.7	24	0.091	0.093	0.099	0.063	0.11
		0.10	0.093	0.099	0.069	0.096
10.0	24	0.10	0.099	0.093	0.088	0.10
		0.10	0.11	0.093	0.087	0.074
7.7	38	0.10	0.10	0.093	0.088	0.087
		0.10	0.092	0.075	0.071	0.060
10.0	38	0.097	0.084	0.075	0.071	0.071
		0.10	0.088	0.075	0.071	0.065
7.7	38	0.085	0.10	0.072	0.047	0.062
		0.089	0.090	0.072	0.059	0.037
10.0	38	0.087	0.096	0.072	0.053	0.049
		0.056	0.051	0.035	0.016	<0.001
		0.056	0.046	0.033	0.010	<0.001
		0.056	0.049	0.034	0.013	<0.001

^a Concentration in parts per million. ^b Averages.

perature of 27 $^{\circ}$ C, Dimilin has a retention time of 5 min.

Extraction of Dimilin from Water. Tap water and field waters collected from mosquito breeding habitats (pastures, ponds, dairy drains, and sewage lagoons) were fortified with ethanolic solutions of Dimilin to give 0.10, 0.05, and 0.01 ppm. Duplicate 600-ml samples of each were partitioned against 3 \times 200 ml aliquots of dichloromethane (freshly distilled); these were dried over anhydrous Na₂SO₄ and the combined aliquots were reduced to dryness in a rotary vacuum evaporator. The residues were dissolved in either 1 or 5 ml of absolute ethanol, and 5 μ l samples were subjected to HPLC.

Stabilization of Dimilin in Water Samples. Since field water samples would be collected at distant locations

Table IV. Stability of Dimilin Films on Glass Plates Exposed to Direct Sunlight (in Percent Recovery)

	h in direct sunlight			
	0	3	6	9
	100.0	98.99	92.12	89.25
	100.0	94.62	87.27	86.02
Averages	100.0	96.77	89.70	87.63

Table V. Recovery of Dimilin from Water Containing Straw

Test no.	Straw, g	Water		Straw, 18 h
		24 h	48 h	
1	0	0.074 ^a		
		0.080		
1	1.5	0.077 ^b		
		0.035		
1	3.0	0.034		
		0.018		
2	0	0.017		
		0.018		
2	0	0.081	0.071	
		0.089	0.071	
2	0.5	0.085	0.071	
		0.061	0.054	
2	1.0	0.061	0.054	
		0.052	0.045	
2	1.5	0.055	0.044	
		0.054	0.045	
2	2.0	0.050	0.044	
		0.052	0.043	
3	3.0	0.051	0.044	
		0.046	0.043	
		0.048	0.041	
		0.047	0.042	
				0.012
				0.011
				0.012

^a Concentration in parts per million. ^b Averages.

and at times and places when immediate extractions could not be made, it was imperative to define the potential losses of Dimilin during the sample holding period. As the pH of the field waters in the test areas varies from about 8 to 10, the loss of Dimilin in holding samples in this range was also important. Duplicate samples of water (600 ml each) which had a pH of 7.7 or were adjusted to 10.0 with NaOH were fortified with 0.1 ppm of Dimilin; 200 ml of dichloromethane was added to each followed by vigorous shaking. These samples were then held at room temperature for either 48 or 144 h and then analyzed.

The Combined Effect of Temperature and pH on Dimilin in Tap Water. Sixty samples of 600 ml of tap

water (30 at pH 7.7 and 30 at pH 10.0) were fortified with Dimilin to 0.1 ppm. These were then placed in temperature-controlled incubators set at 10, 24, and 38 °C (this range of water temperature occurs in field waters where Dimilin may be used) and held in the dark. After 24, 48, 72, 144, and 216 h, duplicate samples were removed from each incubator, extracted, and analyzed. The pH values of water samples were monitored to ensure that there were no appreciable changes during the tests; open pans of water were held in the incubators to minimize evaporation of water from the samples during the holding period.

Stability of Dimilin to Sunlight. Duplicate sets of 140-mm petri dishes were treated with 30 mg of technical Dimilin in ethanol. The ethanol was evaporated with dry nitrogen and the plates were placed outdoors so that the films were exposed to direct sunlight for 0 (immediate extraction with no exposure), 3, 6, and 9 h. At the end of each exposure period, each plate was washed with 100 ml of dichloromethane and then analyzed for Dimilin. Negligible loss due to volatilization was expected, based on vapor pressure data provided by the manufacturer.

In addition, duplicate sets of 600 ml of tap water, held in 1000-ml beakers at pH 7.7 and pH 10.0, were fortified with 0.1 ppm of Dimilin and kept outdoors in direct sunlight on a clear, warm day for 8 h under ambient conditions ranging from 17 to 31 °C. Along with those above, a second set was held outdoors, but with cooling. The cooled samples were placed in an ice bath at 12 ± 1 °C during the same period. At the end of the holding period, each sample was extracted and analyzed.

Stability of Dimilin to Microorganisms. Since many mosquito breeding habitats contain polluted waters, the stability of Dimilin to microbial decomposition is of interest. A water sample from a large sewage lagoon was collected and divided into two portions. One portion was left untreated and the second was boiled to eliminate microbial activity and then cooled to room temperature. Duplicate 600-ml sets of boiled and unboiled water were fortified with 0.1 ppm of Dimilin and then extracted immediately (0 h) or held for 6 and 24 h under ambient conditions prior to extraction and analysis.

Adsorption of Dimilin onto Straw. Duplicate sets of 600-ml tap water samples in 1000-ml beakers were fortified with 0.1 ppm of Dimilin and 0, 1.5, or 3.0 g of straw (stems of dried pasture grasses) were added. These samples were held at 21 °C in the dark for 24 h. After the holding period the sample was passed through a fiberglass filter mat to remove straw fragments and then the water was extracted and analyzed. A second test was run as above except that 0, 0.5, 1.0, or 2.0 g of straw was used and sets of samples were held for 24 and for 48 h. In a third test, duplicate sets of 600 ml of tap water were treated with 0.1 ppm of Dimilin, 3.0 g of straw was added to each, and the samples were held at 21 °C for 18 h; the straw was filtered out as above, washed with 4 × 25 ml of tap water, and held under suction for 5 min. The straw and filter mat

Table VI. Distribution of Dimilin Formulations in Pond Water (in ppm)

Formulation	Sample location	h after treatment								
		1	24	48	72	96	120	144	168	192
Tech. ^a	Top	0.25 ^b	0.14	0.079	0.041	0.027	0.012	0.0066	0.0026	0.0029 ^c
	Bottom	0.051	0.024	0.028	0.023	0.017	0.014	0.0061	0.0023	
25% WP ^d	Top	0.076	0.032	0.029	0.021	0.014	0.0080	0.0034	0.0018	0.0023
	Bottom	0.076	0.033	0.026	0.024	0.015	0.012	0.0029	0.0023	
FL ^e	Top	0.080	0.072	0.054	0.027	0.017	0.011	0.0051	0.0025	0.0029
	Bottom	0.072	0.038	0.026	0.019	0.014	0.012	0.0044	0.0030	

^a Technical. ^b Average of duplicate samples. ^c Insufficient water depth to allow top and bottom samples. ^d 25% wettable powder. ^e Flowable liquid (2.07 lb of AI/gal).

Table VII. Residues of Dimilin in Field Water Samples from 1975 Tests

Field test no.	Date (1975)	Formulation + habitat	Rate (lb of AI/acre)	Sample collection time ^a				
				Pre-treatment	1	24	48	72
75-1	5/15	25% WP, ^b pasture	0.02	ND	0.0016 ^c	ND ^d	ND	ND
				ND	0.0015	ND	ND	ND
				ND	0.0027	ND	ND	ND
				ND	ND	ND	ND	ND
75-3	5/20	25% WP, periphery of alkaline lake	0.1	ND	0.0019 ^e	ND	ND	ND
				ND	0.013	ND	ND	ND
				ND	0.0036	ND	ND	ND
				ND	0.011	ND	ND	ND
				ND	0.017	ND	ND	ND
				ND	0.0027	ND	ND	ND
75-4	6/12	25% WP, pasture	0.04	ND	0.0082	ND	ND	ND
				ND	0.058	0.0016	0.0021	ND
				ND	0.038	0.0018	0.0045	ND
				ND	0.031	0.0038	0.0025	ND
75-5	6/17	25% WP, pasture	0.02	ND	0.075	0.0067	0.0028	ND
				ND	0.050	0.0035	0.0030	ND
				ND	0.0059	ND	ND	ND
				ND	0.0037	0.0013	ND	ND
75-6	6/20	25% WP, pasture	0.04	ND	0.0045	ND	ND	ND
				ND	0.0040	0.0013	ND	ND
				ND	0.031	0.0035	0.0014	ND
				ND	0.032	0.0042	0.0016	0.0015
75-9	7/1	25% WP, pasture	0.04	ND	0.025	0.0031	0.0013	ND
				ND	0.021	0.0045	0.0054	ND
				ND	0.027	0.0025	0.0021	0.0026
				ND	0.021	0.0043	ND	0.0014
75-13	7/16	25% WP, pasture	0.02	ND	0.025	0.0053	0.0023	0.0010
				ND	0.023	0.0036	0.0030	0.0020
				ND	0.0052	ND	ND	ND
				ND	0.0013	0.0015	ND	ND
75-14	7/17	25% WP, pasture	0.04	ND	0.0087	0.0016	ND	ND
				ND	0.011	ND	ND	ND
				ND	0.0095	0.0015	ND	ND
				ND	0.012	0.0069	ND	ND
75-23	8/13	FI, ^f dairy drain	0.04	ND	0.012	0.0069	0.0024	ND
				ND	0.0088	ND	ND	ND
				ND	0.016	ND	ND	ND
				ND	0.015	ND	ND	ND
75-25	8/19	25% WP, pasture	0.02	ND	0.0063	ND	ND	ND
				ND	0.012	ND	ND	ND
				ND	0.0075	ND	ND	ND
				ND	0.0017	ND	ND	ND
75-26	8/19	FL, dairy drain	0.1	ND	0.0037	ND	ND	ND
				ND	0.0043	ND	ND	ND
				ND	1.39	0.0022	0.0016	ND
				ND	0.76	0.0066	0.0029	ND
75-28	8/27	FL, dairy drain	0.11	ND	0.72	0.0052	0.0022	ND
				ND	0.98	0.0040	0.0027	ND
				ND	0.96	0.0045	0.0024	ND
				ND	0.016	ND	ND	ND
75-30	9/1	1.0% G, ^g pasture	0.032	ND	0.014	ND	ND	ND
				ND	0.020	ND	ND	ND
				ND	0.048	ND	ND	ND
				ND	0.024	ND	ND	ND
75-30	9/1	1.0% G, ^g pasture	0.032	ND	0.024	ND	ND	ND
				ND	ND	ND	ND	ND
				ND	0.0070	0.0045	ND	ND
				ND	ND	ND	ND	ND

Table VII (Continued)

Field test no.	Date (1975)	Formulation + habitat	Rate (lb of AI/acre)	Pre-treatment	Sample collection time ^a			
					1	24	48	72
75-31	9/6	0.5% G, pasture	0.023	ND ND	0.0070 ^e	0.0045	ND	ND
					0.0059	ND	ND	ND
					0.011	ND	ND	ND
					0.0036	ND	ND	ND
					0.0040	ND	ND	ND
					0.0060 ^e	ND	ND	ND

^a In hours after treatment. ^b 25% wettable powder. ^c Parts per million (not corrected for recoveries). ^d ND, not detected (<0.001 ppm). ^e Averages. ^f Flowable liquid (2.07 lb of AI/gal). ^g Granules.

were placed in a Waring blender with 200 ml of dichloromethane and 5 g of anhydrous Na₂SO₄ and blended for 3 min. The liquid mixture was passed through a fiberglass filter and the filtrate washed with 4 × 50 ml of dichloromethane. The combined solvent washes were reduced to dryness and dissolved in ethanol for HPLC.

Distribution of Dimilin Formulations in Pond Water. Since it is known that the persistence and distribution of chemical control agents will vary with the type of formulation applied (Schaefer and Dupras, 1973), it was of importance to study the distribution of available formulations of Dimilin. Knowledge of the distribution is important in order to develop methods for sampling field waters. Three treatments were made to 1-m² outdoor ponds filled with 70 gal of water each: technical material (applied in 20 ml of ethanol), 25% wettable powder (applied in 30 ml of water), and 2.07 lb of active ingredient (AI)/gal of flowable liquid (applied in 30 ml of water). All treatments were calculated to give an initial concentration of 0.1 ppm. At 1 h after treatment and then at 24-h intervals for 8 days, duplicate 600-ml water samples were taken from both the top and bottom 2 in. of each pond; these were extracted and analyzed by HPLC.

Decomposition of Dimilin in Water. In order to determine whether or not the reduction of Dimilin concentration in water with time was due to decomposition rather than adsorption, *p*-chlorophenylurea, a breakdown product (Metcalf et al., 1975), was monitored along with the parent compound. For recovery determinations, duplicate samples of 600 ml each of tap water were fortified with *p*-chlorophenylurea to give concentrations of 0.10, 0.05, and 0.01 ppm; 200 ml of acetonitrile was added to each sample, followed by vigorous shaking and extraction with 3 × 200 ml of ethyl acetate. The ethyl acetate extract was dried over anhydrous Na₂SO₄ and reduced to dryness and the residues were dissolved in ethanol and analyzed by HPLC. The conditions for HPLC were the same as for Dimilin except that the mobile phase was 30% methanol-70% water. The retention time for *p*-chlorophenylurea was 7 min at 27 °C.

A 1-m² outdoor pond containing 70 gal of water was treated with technical Dimilin to give a calculated initial concentration of 0.1 ppm. At 1 h and 1, 2, 3, and 4 days following treatment, four 600-ml water samples were taken from the upper 2 in. of the water body. Two of these were analyzed for Dimilin and two for *p*-chlorophenylurea, as described above.

Residues of Dimilin in Field Water Samples from 1975 Tests. During the 1975 field trials of Dimilin, as a mosquito control agent, 600-ml water samples were collected just before (usually two samples) and at 1, 24, 48, and 72 h following treatment (usually four samples at each interval). A summary of these tests is given in Table I.

Details of methods for field applications were as previously described (Schaefer and Wilder, 1972, 1973). Following one aerial application, 600-ml water samples were collected at 24 and 48 h after treatments and extracted and analyzed for *p*-chlorophenylurea to determine if this by-product formed under actual field conditions.

Release of Dimilin from 0.5 and 1.0% Granules. In field tests 75-30 and 75-31, 1.0 and 0.5% Dimilin granules were applied by air, respectively. The aircraft used was calibrated to deliver 3.2 lb of the 1.0% granules/acre (0.032 lb of AI/acre) and 4.5 lb of the 0.5% granules (0.023 lb of AI/acre). It was important to determine the rate at which Dimilin is released from these granules following their entry into water. Twelve 1-gal jars containing 3000 ml of tap water each were treated with Dimilin granules to give an initial concentration of 0.1 ppm (6 jars with 0.5% and 6 with 1.0% granules). At the end of 1, 8, 24, 96, and 144 h, one each of the jars treated with the 0.5% and 1.0% granules was filtered to remove solids, and duplicate 600-ml aliquots of water were extracted and analyzed for Dimilin.

RESULTS AND DISCUSSION

Recovery of Dimilin from Water. Table II shows the recoveries of Dimilin from tap, pasture, pond, dairy drain, and sewage lagoon water. Recoveries from tap, pasture, and pond waters were 97% or better, and using the 600-ml sample size, it was possible to estimate Dimilin concentration to a detection limit of 0.001 ppm (minimum peak was twice background). Reduced recoveries occurred in water having a greater content of organic matter, e.g., dairy drain and sewage water, presumably through adsorption.

Stabilization of Dimilin in Water Samples. A Dimilin concentration of 0.1 ppm in water is stabilized following the addition of dichloromethane. There is only 1-2% loss at 48 h and 6-7% at 144 h. Thus, it appears that if field samples are stabilized with dichloromethane, immediately after collection, they can be held for 24 to 48 h with only small losses within the pH range of 7.7-10.0.

Effects of Temperature and pH on the Stability of Dimilin in Water. Table III shows the results of varying pH and temperature of tap water samples fortified with 0.1 ppm of Dimilin. There was no apparent effect due to pH at 10 °C nor between the 10 °C temperature and pH 7.7 samples held at 24 °C. It is apparent that the compound is less persistent as pH and temperature increase, especially when both these values are high (38 °C).

Stability of Dimilin to Sunlight. When Dimilin films on glass were placed in intense, direct sunlight, there was a gradual loss that reached about 12% after 9 h exposure (Table IV); a small loss may have been due to volatilization, which was not measured. This indicates a fairly good photostability of the technical material in comparison

to light-sensitive pesticides (Schaefer and Dupras, 1973). When water was treated with 0.1 ppm and held for 8 h in direct sunlight at pH 7.7 and 10.0, there was only a 3–5% loss at either pH for cooled samples. A 4% loss of uncooled samples was observed at pH 7.7, but a 22% loss occurred at pH 10.0. Thus, sunlight apparently does not directly cause high reduction in persistence, but the higher water temperature at higher pH levels is an important factor. This is very significant under field conditions since many pastures, and other alkaline habitats, have water pH levels of about 10.0, and water temperatures frequently rise to 38 °C in the daytime, during summer conditions.

Stability of Dimilin to Microorganisms. Microorganisms had little, if any, effect on the concentration of Dimilin in polluted water. A 14–15% reduction from the 0.1-ppm initial concentration was found immediately following treatment, and subsequent losses of 30% at 6 and 42% at 24 h appear to be due to adsorption since there were no differences between boiled and unboiled sewage waters (also see Table II). This conclusion is in agreement with the report of Metcalf et al. (1975) who found no degradation by the soil microorganism, *Pseudomonas putida*.

Adsorption of Dimilin onto Straw. Table V shows the recoveries of Dimilin from tap water containing different amounts of straw and held for 24 and 48 h at 21 °C in the dark. The recoveries diminish as the amount of straw or the holding time increases. Extraction of the straw after 18-h exposure (test 3) shows that Dimilin is present and the losses are partly, if not largely, due to adsorption. This confirms other evidence of adsorptive losses previously discussed (Table II). Carringer et al. (1975) studied the adsorption of Dimilin and other pesticides onto soil organic matter and concluded that adsorption appeared to be inversely related to the water solubility of the compound; they reported a water solubility of 0.3 ppm for Dimilin.

Distribution of Dimilin Formulations in Pond Water. Table VI shows the distribution of Dimilin in the upper and lower levels of 70-gal, 1-m² ponds. Application of the wettable powder results in a homogeneous distribution, even at the 1-h sampling time. However, when either technical Dimilin in ethanol or the flowable liquid formulation was applied, the concentration of active ingredient in the upper water level was much greater than the bottom for up to 3 days. This finding is significant for determining the selection of where water samples will be taken for residues. Also, since some mosquito larvae are browse feeders and feed primarily on the bottom, and others are filter feeders and feed near the surface (Pucat, 1965), the type of formulation applied might affect control results.

Decomposition of Dimilin in Water. Recoveries of *p*-chlorophenylurea from tap water, using the extraction methods described, were 99% at 0.1, 100% at 0.05, and 95% at 0.01 ppm. Figure 1 shows that in outdoor pond water as the concentration of Dimilin decreases, the concentration of *p*-chlorophenylurea increases and apparently is a major hydrolysis product. Thus, the reduction of Dimilin concentration in water with time is due to hydrolysis as well as to adsorption.

Residues of Dimilin in Field Water Treated during 1975 Tests. Table VII shows the residues of Dimilin in water from various mosquito breeding habitats where experimental applications were made (Table I). Applications of 0.04 lb of AI/acre to pastures gave excellent mosquito control, and residues could be measured usually until 48 h, but there was very limited persistence at 72 h.

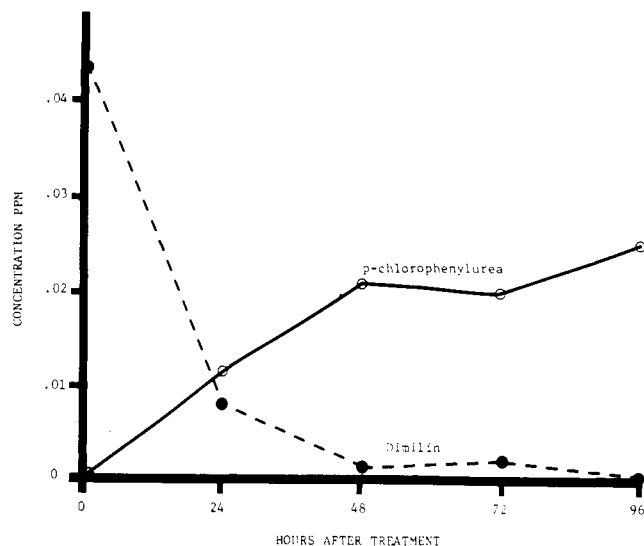


Figure 1. The breakdown of Dimilin to *p*-chlorophenylurea in outdoor pond water.

On pastures treated with 0.02 lb of AI/acre the treatment gave approximately 80% mortality of the field populations, and residues in water usually could not be measured beyond 24 h. A border application (about 6 acres of the shoreline of a 100-acre water body) of 0.1 lb of AI/acre to a very alkaline lake resulted in very low initial concentration and very limited residual (field test no. 75-3). The short residual was undoubtedly due to dilutions as well as to the harsh conditions of this habitat. Tests on dairy drains gave from good (field test no. 75-26) larval control along with detectable residues to almost no control (field test no. 75-28) and very limited residues. It is important to note that these results are directly correlated with the amount of organic debris present in the habitat at the time of treatment and during the post-treatment sampling period. Some dairy drains, e.g., field test no. 75-28, have large amounts of fresh dairy wastes that are continually being pumped into the sump and are fairly evenly distributed; the potential for loss via adsorption and dilution is extreme and presumably accounts for the results. Many dairy drains have dense vegetation within several feet of the bank. Since mosquito larvae and pupae are mainly found near the vegetation, this perimeter area requires a greater dose than for other parts of the pond. In field test no. 75-26, the above situation occurred and the perimeter was sprayed to a much greater extent than the mid-section of the drain; this resulted in much higher initial residues (Table VII) as well as in good control. (Note: Water residue samples were collected from the same perimeter areas where immature mosquitoes occurred.)

In field test no. 75-4, water samples taken at 24 and 48 h showed 0.029 and 0.019 ppm of *p*-chlorophenylurea, respectively. Thus, this breakdown product also occurs under natural field conditions and hydrolysis of Dimilin is one factor limiting its persistence.

Poor mosquito control was obtained with the 1.0% granular application and the residues in water were very limited (field test no. 75-30), but good control resulted from application of the 0.5% granules, and all of the water samples collected at 1-h post-treatment showed residues (field test no. 75-31). Table VIII shows the release of Dimilin from the 1.0 and 0.5% granules. It is apparent that only a partial release occurs, especially with the 1.0% granules, and in spite of the quantity of active ingredient applied, only a limited amount actually entered the water. Initial release from the 0.5% granules was 35% in com-

Table VIII. Release of Dimilin from 0.5 and 1.0% Granules

Formulation + rate	h after treatment					
	1	8	24	48	96	144
1.0% granules	0.023 ^a	0.020	0.025	0.032	0.037	0.037
at 0.1 ppm	0.021	0.023	0.032	0.032	0.041	0.035
	0.022 ^b	0.022	0.029	0.032	0.039	0.036
0.5% granules	0.034	0.033	0.028	0.030	0.039	0.027
at 0.1 ppm	0.036	0.032	0.028	0.039	0.050	0.035
	0.035	0.032	0.028	0.035	0.045	0.031

^a Concentration in parts per million. ^b Averages.

parison to only 22% from the 1.0% granules and this difference may account for differences in the field results. Thus, when granular formulations are used, it is very important when attempting to correlate control and residues to measure the actual release rate of the granules applied.

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Role of Water in the Hydrolysis of Parathion and Methylparathion on Kaolinite

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Oven-dried kaolinite has a catalytic effect upon parathion and methylparathion hydrolysis. Addition of water to kaolinite, in the limits of sorbed water, affected the degradation kinetics of both insecticides and increased the degradation rate. A slight increase in the moisture content above that corresponding to sorbed water results in a steep decrease in the degradation rate. Following hydrolysis, part of the organophosphate hydrolysis product is fixed at the clay surface. The data obtained suggest that water molecules associated with the exchangeable cations participate in the hydrolysis.

The sorption of organic molecules by clay surfaces is one of the most studied aspects of the clay-organic interactions. Almost all the studies of the sorption of organics by clays point out the decisive role of the hydration level of the system on the sorption process (e.g., see Yariv et al., 1966; Mortland and Meggit, 1966). The sorbed organic molecules may undergo several kinds of reactions as a result of the catalytic effect of the clay surfaces.

Catalytic reactions on clay surfaces have received considerable attention, but information on the role of water in these reactions is scarce (Rosenfield and Van Valkenburg, 1965; Solomon and Murray, 1972). Most of the older studies were undertaken on dehydrated systems and at high temperatures, and only recently was it observed that catalytic reactions could also occur at low temperatures and at relatively high hydration levels (Mortland, 1970).

In a previous work (Saltzman et al., 1974) it was shown that kaolinite has a catalytic effect upon parathion degradation at room temperature. The degradation products were *p*-nitrophenol and an alkyl thiophosphate. The same hydrolysis occurred with methylparathion. The degradation rate was dependent on the nature of the saturating cation, and the process was hindered by the presence of free water. As the degradation rate on oven-dried clays was much slower with Na- than with Ca-kaolinite, it was suggested that the determining factor could be the presence of cation hydration water on clays, that is, the capacity of the different cations to retain their hydration shell, when dried at 105 °C.

In a recent study of pirimiphos ethyl, another bioactive phosphate thioester (Mingelgrin et al., 1975), catalytic activity of kaolinite at room temperature was also noted. Additional sorbed water in Na-kaolinite enhanced the catalytic effect of the clay, as compared with that of the oven-dried clay. The presence of free water, on the other hand, drastically reduced the chemical conversion of parathion on kaolinitic soils (Yaron, 1975).

Knowledge concerning the effect of water content on the degradation of organic molecules in an adsorbed state is important, as it may shed light on the mechanism of the process. From a practical point of view, it may clarify some

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