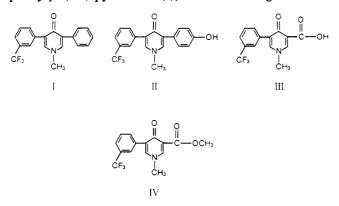
# Bioconcentration and Field Dissipation of the Aquatic Herbicide Fluridone and Its Degradation Products in Aquatic Environments

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The accumulation and dissipation patterns of the aquatic herbicide fluridone, 1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone, and its major degradation products have been determined in 40 pond and lake experiments in the United States, Panama, and Canada. The average bioconcentration factor for the total residue of fluridone plus a single major metabolite, 1-methyl-3-(4-hydroxyphenyl)-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone, in several fish species was 1.33, 7.38, and 6.08 in edible tissue, inedible tissue, and whole body, respectively. Fluridone dissipated with an average half-life of 20 days in pond water and 3 months in pond hydrosoil. The treatment of small areas (0.8-4.0 ha) of large lakes resulted in more rapid dissipation due to dispersal of fluridone into the surrounding untreated water. Little or no carry-over of residues occurred prior to annual retreatments of the ponds. Mathematical models were evaluated for relating the half-life of fluridone in pond water to physical and chemical properties of the water.

Fluridone, 1-methyl-3-phenyl-5-[3-(trifluoromethyl)-phenyl]-4(1H)-pyridinone (I), is the active ingredient in



the experimental aquatic herbicide, SONAR. A single annual application of SONAR has resulted in the management of troublesome vascular aquatic weeds at low application rates (McCowen et al., 1979; Sanders et al., 1979; Arnold, 1979; Parka et al., 1978; Grant et al., 1979; Rivera et al., 1979).

Studies with  $[{}^{14}C]$  fluridone have been conducted to identify metabolites and degradation products. These studies have resulted in the identification of 1-methyl-3-(4-hydroxyphenyl)-5-[3-(trifluoromethyl)phenyl]-4-(1H)-pyridinone (II) as a major metabolite comprising greater than 10% of the total radioactivity in fish (Rainey and Berard, 1979). The same metabolite was also identified as a minor metabolite in water and hydrosoil (Muir and Grift, 1982). The 2-hydroxyphenyl isomer of II has been identified as a minor metabolite comprising less than 10% of the total radioactivity in fish (Rainey and Berard, 1979) and in water and hydrosoil (Muir and Grift, 1982).

A single major hydrosoil metabolite, 1,4-dihydro-1methyl-4-oxo-5-[3-(trifluoromethyl)phenyl]-3-pyridinecarboxylic acid (III), was very slowly formed in the hydrosoil of water-sediment systems maintained for several months in the laboratory (Rainey and Berard, 1979; Marquis et al., 1982; Muir and Grift, 1982). However, III was not detected in the hydrosoil of small outdoor ponds exposed to natural sunlight (Rainey and Berard, 1979; Muir and Grift, 1982).

<sup>14</sup>C aqueous photolysis studies have indicated that the parent compound is the only major residue present in treated water. The fluridone molecule is very extensively photodegraded to several low molecular weight fragments (Saunders and Mosier, 1983). The photoproducts appear to rapidly dissipate from the water by volatilization so that significant levels do not accumulate in the water (Lilly Research Laboratories, 1981; Muir and Grift, 1982). Fluridone does not hydrolyze in aqueous solution (Lilly Research Laboratories, 1981).

Based upon the results of the  $^{14}$ C metabolism and degradation studies, residue methods have been developed for determining the major residues which might be expected to occur under actual field conditions. These methods include the determination of fluridone in water and hydrosoil (West, 1978; West and Parka, 1981), fluridone plus III in hydrosoil (West, 1983), and fluridone plus II in fish (West and Burger, 1980).

The dissipation of fluridone from water, aquatic plants, hydrosoil, and fish has previously been reported for field experiments in the United States (West et al., 1979; West and Parka, 1981), Panama (Sanders et al., 1979), and Canada (Muir et al., 1980; Muir and Grift, 1982). However, the accumulation and dissipation of the major degradation products of fluridone have not yet been described. The primary purpose of this paper is to summarize the bioconcentration and field dissipation of fluridone and its major metabolites in 40 pond and lake trials. A secondary objective is to develop a mathematical model for predicting the half-life of fluridone in pond water based upon the physical and chemical properties of the water.

## EXPERIMENTAL SECTION

Methods of SONAR Application and Descriptions of Field Trials. Fluridone was formulated as a 5% clay pellet (SONAR 5P) or as an aqueous suspension containing 4 lb of fluridone/gal (SONAR 4AS) or 50% fluridone (SONAR 50AS). SONAR 5P was uniformly surface applied to the water from a boat with a granular applicator and the pellets sank to the hydrosoil or into the weed biomass. Two different methods of application were evaluated for the AS formulations. With the first technique, SONAR diluted with water was surface applied by spraying onto or just below the water surface. The second method utilized a bottom application in which the AS diluted with water was sprayed along the bottom of the

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#### Table I. Description of SONAR Field Dissipation Trials

			SONAR a	lake or pond	l description		
location	type	formulation	kg/ha	method <sup>a</sup>	date	depth, m	size, ha
Hialeah, FL	pond	4AS	1.68	BA	9/28/77	5.2	0.36
Hialeah, FL	pond	4AS	1.12	BA	9/28/77	5.2	0.78
Deiray Beach, FL	pond	4AS	1.12	BA	5/11/78	1.2	0.10
Crystal River, FL	pond	4AS	1.12	SA	5/12/80	1.2	0.18
Crystal River, FL	pond	4AS	1.12	BA	5/12/80	1.7	0.32
Irving, TX	pond	4AS	1.12	BA	5/23/78	1.2	0.77
Memphis, TN	pond	4AS	1.12	BA	6/13/78	0.9	1.22
Monterey, CA	pond	4AS	1.12	BA	6/14/78	1.8	0.15
Hedgesville, WV	pond	4AS	0.84	BA	6/23/78	0.9	0.15
Seymour, IN	pond	4AS	0.84	BA	6/13/79	0.9	0.37
Seymour, IN	pond	4AS	0.84	$\mathbf{SA}$	6/13/79	0.9	0.37
Sandborn, IN	pond	4AS	1.12	$\mathbf{SA}$	6/24/80	1.9	0.61
Sandborn, IN	pond	4AS	1.12	BA	6/24/80	1.0	0.49
Weldon Springs, MO	pond	4AS	1.12	BA	6/26/78	0.6	0.17
Lake City, MI	pond	4AS	1.12	$\mathbf{SA}$	6/2/76	1.1	0.04
Ithaca, NY	pond	4AS	0.90	BA	5/24/77	0.7	0.07
Manotick, Canada	pond	50AS	1.12	$\mathbf{SA}$	6/2/80	1.5	0.09
Crystal River, FL	pond	5P	1.12	$\mathbf{SA}$	5/12/80	1.9	0.32
Boca Raton, FL	pond	5P	1.12	$\mathbf{SA}$	5/22/80	1.4	0.34
Irving, TX	pond	5P	1.12	$\mathbf{SA}$	5/16/78	1.8	0.17
Sandborn, IN	pond	5 <b>P</b>	1.12	$\mathbf{SA}$	6/24/80	1.2	0.85
Weldon Springs, MO	pond	5P	1.12	$\mathbf{SA}$	6/27/78	2.0	0.13
Manotick, Canada	pond	5P	1.12	$\mathbf{SA}$	6/2/80	1.5	0.09
Lake Pierce, FL	lake	4AS	2.24	$\mathbf{SA}$	5/7/80	2.0	4.0
Lake Pierce, FL	lake	4AS	2.24	BA	5/7/80	2.0	4.0
Lake Pierce, FL	lake	5P	2.24	$\mathbf{SA}$	5/7/80	2.0	4.0
Lake Gatun, Panama	lake	4AS	1.68	BA	1/12/78	4.6	0.81
Lake Gatun, Panama	lake	4AS	1.68	BA	1/12/78	6.9	0.81
Lake Gatun, Panama	lake	5P	1.68	$\mathbf{SA}$	1/12/78	5.7	0.81
Lake Gatun, Panama	l <b>ak</b> e	$5\mathbf{P}$	1.68	$\mathbf{SA}$	1/12/78	5.9	0.81

<sup>*a*</sup> SA = surface application; BA = bottom application.

Table II. Half-Life  $(t_{1/2})$  of Fluridone in Pond Water Treated with SONAR 4AS

		physical and chemical properties <sup>a</sup>								
		tem	p, °C		turbidity,	TDS,b	secchi		DO, <sup>c</sup>	t <sub>1/2</sub> ,
deg latitude	location	air	water	$_{\rm pH}$	NTU	ppm	disk, m	color	ppm	days
24-28	Hialeah, FL	NA <sup>d</sup>	NA	NA	NA	NA	NA	NA	NA	60
	Hialeah, FL	NA	NA	NA	NA	NA	NA	NA	NA	50
	Delray Beach, FL	27.5	27.7	7.2	2.3	378	0.8	15	2.2	13
28 - 32	Crystal River, FL	29.9	27.3	8.2	1,3	658	0.8	41	5.6	5
	Crystal River, FL	31.9	28.6	8.8	14.2	176	0.7	55	8.9	12
32-36	Irving, TX	30.2	26.0	9.0	4.2	414	0.6	49	5.5	6
	Memphis, TN	25.2	27.7	6.5	11.9	175	0.5	187	2.2	46
36-40	Monterey, CA	15.4	20.7	7.8	1.5	594	1.4	36	4.3	17
	Hedgesville, WV	26.4	22.7	6.8	4.2	67	1.2	56	7.0	6
	Seymour, IN	22.5	24.2	8.6	6.0	190	0.8	20	8.2	16
	Seymour, IN	23.1	24.7	8.0	5.2	342	0.5	28	5.8	16
	Sandborn, IN	24.6	26.0	8.9	0.7	198	1.7	20	6.2	8
	Sandborn, IN	25.6	26.4	9.0	1.2	375	1.0	20	5.4	9
	Weldon Springs, MO	30.2	29.4	6.8	11.8	129	0.6	43	5.6	47
40-44	Lake City, MI	NA	NA	NA	NA	NĀ	NA	NA	NA	5
	Ithaca, NY	NA	NA	NA	NA	NA	NA	NA	NA	11
44-48	Manotick, Canada	NA	NA	NA	NA	NA	NA	NA	NA	21

 $^{a}$  Average values for observations taken on dates of residue sample collection during the first month after treatment.  $^{b}$  Total dissolved solids.  $^{c}$  Dissolved oxygen (average of measurements at the top and bottom of the water column).  $^{d}$  Information not available.

lake or pond from a boat with trailing, weighted hoses. Dissipation trials were conducted under actual field use conditions, and descriptions of the treated ponds are contained in Tables I and II. In the United States, pond trials (1.2 ha or smaller) were located in Florida, West Virginia, Tennessee, Missouri, Texas, California, Indiana, Michigan, and New York (McCowen et al., 1979; Arnold, 1979; Parka et al., 1978; Grant et al., 1979; Rivera et al., 1979; West and Parka, 1981). The Canadian pond trial was located in Ontario. The entire pond was treated in each trial.

Lake trials were conducted in Gatun Lake of the Panama Canal (Sanders et al., 1979) and in Lake Pierce, Florida. Small areas (0.8-4.0 ha) of the large lakes were treated.

**Residue Sample Collection and Analysis.** Samples of water, hydrosoil, and fish were collected, prepared, and analyzed according to published procedures (West, 1978; West et al., 1979; West and Burger, 1980; West and Parka, 1981). Fish samples were filleted and separated into edible (muscle) and inedible tissue. The determination of the degradate (III) in hydrosoil was accomplished with a modification of the fluridone hydrosoil residue method (West and Parka, 1981) in which a methyl ester derivative (IV) was formed by reaction with diazomethane and measurement was accomplished by high-pressure liquid

Table III.Summary of Fluridone Dissipation Data inPond and Lake Water followingApplications of SONAR AS

body of	time after	no. of	ppm of fluri	done
water	treatment	trials	range	av
pond	1 day	14	0.035-0.112	0.087
	3 days	16	0.016 - 0.114	0.069
	1 week	17	0.016-0.104	0,057
	2 weeks	17	0.006-0.092	0,043
	3 weeks	3	0.022 - 0.044	0.035
	1 month	17	0.002-0.075	0.029
	2 months	17	NDR <sup>a</sup> -0.046	0.014
	3 months	5	NDR-0.023	0.009
	4 months	16	NDR-0.019	0.006
	6 months	8	NDR-0.001	0.002
	12 months	9	NDR-0.004	0.001
lake	1 day	2	0.012 - 0.039	0.026
	1 week	4	0.004 - 0.012	0.008
	2 weeks	4	0.003-0.007	0.006
	3 weeks	2	NDR-0.001	0.001
	1 month	2	NDR-0.001	0.001
	2 months	2	NDR	NDR
	3 months	$\overline{2}$	NDR-0.005	0.003

<sup>a</sup> No detectable residue at a detection limit of approximately 0.001-0.005 ppm.

chromatography with UV detection at 313 nm (West, 1983).

Hydrosoil residue data were converted from ppm to kg/ha in order to relate residue levels to the application rates. Residues were converted to kg/ha according to the equation

residue (kg/ha) = (ppm  $\times$  W)/(nr<sup>2</sup>  $\times$  31.8)

where W equals the total dry weight (g) of soil collected, n equals the number of soil subsamples collected, and r equals the radius (cm) of the soil sampler probe. The conversion factor, 31.8, converts the amount of fluridone from  $\mu$ g to kg and the total surface area sampled from cm<sup>2</sup> to ha.

#### RESULTS AND DISCUSSION

**Dissipation of Fluridone from Water.** The dissipation of fluridone from water following applications of SO-NAR AS and SONAR 5P is summarized for all of the field trials in Tables III and IV, respectively. With SONAR AS, the average concentration was a maximum at 1 day after treatment (DAT) in ponds (0.087 ppm) and lakes (0.026 ppm). Applications of SONAR 5P resulted in lower initial concentrations of the herbicide in water (Table IV), with the average concentration reaching a maximum of 0.025 ppm 2 weeks after treatment in ponds and 0.022 ppm 1 DAT in lakes.

Applications of SONAR to small plots (0.8-4.0 ha) in large lakes resulted in lower fluridone concentrations and more rapid dissipation than when entire ponds were treated (Tables III and IV). These results were largely due to dispersal of the herbicide into surrounding untreated areas of the lake. In Gatun Lake of the Panama Canal, water from control plots located approximately 0.2 and 0.5 km from the nearest treated plot contained 0.006 and 0.014 ppm 1 DAT, respectively. The fluridone concentration declined to less than 0.003 ppm in both treated and control plots by 21 DAT. In Lake Pierce, Florida, water from a control plot located approximately 0.9 km from the nearest treated plot contained a trace of fluridone (0.005 ppm) 14 DAT.

The half-life for fluridone in pond water treated with SONAR AS ranged from 5 to 60 days with an average of 20 days (Table II). True half-life values could not be

Table IV. Summary of Fluridone Dissipation Data in Pond and Lake Water following Applications of SONAR 5P

body of time after		no, of	ppm of fluridone		
water	treatment	trials	range	av	
pond	1 day	5	NDR <sup>a</sup> -0.016	0.007	
	3 days	6	NDR-0.019	0.008	
	1 week	6	0.007-0.034	0.018	
	2 weeks	6	0.016-0.029	0.025	
	3 weeks	3	0.009-0.026	0.017	
	1 month	6	0.006-0.027	0.018	
	2 months	6	NDR-0.028	0.015	
	4 months	5	NDR-0.020	0.007	
	6 months	3	NDR-0.003	0.001	
lake	1 day	2	0.011-0.032	0.022	
	1 week	3	0.005-0.008	0.007	
	2 weeks	3	0.002-0.005	0.004	
	3 weeks	2	0.001-0.003	0.002	
	1 month	2	NDR-0.002	0.001	
	2 months	2	NDR	NDR	
	3 months	2	NDR	NDR	

<sup>a</sup> No detectable residue at a detection limit of approximately 0.001-0.005 ppm.

estimated for ponds treated with SONAR 5P because the fluridone concentration represented a net value reflecting both dissipation from the water and a gradual release of more herbicide into the water as the clay pellets dissolved. However, the average fluridone concentration in pond water from the SONAR 5P trials was less than or similar to that from the AS trials, and after reaching a maximum concentration 14 DAT, the dissipation rate was similar to that for SONAR AS (Tables III and IV).

True  $t_{1/2}$  values could also not be estimated for lake trials because the dissipation was largely due to dispersal and dilution rather than degradation or hydrosoil adsorption. Dispersal and dilution reduced the apparent half-life in lake water to less than 1 week (Tables III and IV).

Factors Affecting the Half-Life of Fluridone. An attempt was made to construct a predictive equation for the half-life of fluridone in pond water from variables which could potentially affect the dissipation rate. In ponds treated with SONAR AS, the half-life averaged 11 days in 5 trials receiving surface applications and 24 days in 12 ponds receiving bottom applications. However, the method of application is not a critical factor influencing the fluridone half-life (West and Parka, 1981). Since fluridone rapidly disperses throughout the entire water column (Rivera et al., 1979), dissipation mechanisms such as photolysis, plant uptake, and hydrosoil adsorption are not likely to be affected by the application method.

Degradation and metabolism studies have indicated that aqueous photolysis is the primary mechanism for fluridone degradation in aquatic ecosystems (West et al., 1979; Lilly Research Laboratories, 1981; Saunders and Mosier, 1983; Muir and Grift, 1982). Consequently, variables which affect sunlight intensity and/or sunlight penetration may largely govern the dissipation rates. Possible variables are geographic location, date of application, water depth, turbidity, weather, weed cover, dissolved oxygen levels, pH. and the presence of photosensitizing agents in the water. Since these variables are frequently unknown, variable, or difficult to measure under field conditions, the prediction of the fluridone half-life for a given pond is a difficult task. Nevertheless, an effort was made to construct a predictive equation for the half-life by using information available from the ponds.

Geographic location did not consistently influence  $t_{1/2}$  values (Table II). There appeared to be no relationship

Table V. Comparison of Observed Fluridone Half-Lives in Pond Water with Those Predicted from Pretreatment Values for Dissolved Oxygen (DO) and Water Turbidity (T)

			ł	half-life, d <b>a</b> ys			
	pretr <b>e</b> atment data			predicted		prediction error, days	
pond location	$\overline{\mathrm{DO}^a}$	T	obsd	eq 3	eq 4	eq 3	eq 4
Irving, TX	5.8	1.4	6	7	9	1	3
Hedgesville, WV	7.0	3.9	6	8	10	2	4
Weldon Springs, MO	7.8	20.0	47	43		4	
Monterey, CA	7.1	1.3	17	1	8	16	9
Sandborn, IN	7.6	1.5	9	0	8	9	1
Sandborn, IN	8.6	1.0	8	- 5	6	13	2
Seymour, IN	5.0	1.3	16	9	10	7	6
Sevmour, IN	6.7	2.8	16	6	9	10	7
Delray Beach, FL	10.2	8.4	13	6	9	7	<b>4</b>
Memphis, TN	4.8	17.0	46	47		1	
Crystal River, FL	10.6	2,4	12	- 9	5	21	7
Crystal River, FL	3.9	1.9	5	15	12	10	7
						$\overline{X}$ : 8	5

<sup>a</sup> Average of DO levels measured at the top and bottom of the water column.

between pond location (in degrees latitude) and fluridone half-life. In fact, by discounting the atypical half-lives of 50 and 60 days in two of the Florida trials, the average  $t_{1/2}$ was 16 days both north and south of 36° latitude. The two Florida ponds with long half-lives were not typical of the other ponds due to a much greater average water depth (5.2 m), an extremely dense infestation of the aquatic weed hydrilla, and a late-September application date. Each of these factors would be expected to decrease the rate of photodegradation of the herbicide.

It has been suggested that the timing of the herbicide application may affect its rate of dissipation by affecting water temperature and sunlight intensity (Muir and Grift, 1982). Comparing the half-life data in Table II with the dates of application in Table I suggests that this hypothesis may be true. The half-life averaged  $9 \pm 4$ ,  $19 \pm 15$ , and  $55 \pm 7$  days for ponds treated in May, June, and September, respectively.

Water depth can potentially affect dissipation rates by affecting the degree of sunlight penetration. Regressing the half-life  $(t_{1/2})$  of fluridone determined in the 17 ponds (Table II) against the average water depth (Table I) resulted in the equation

$$t_{1/2} \text{ (days)} = 8.2 \text{ WD} + 7.0 \tag{1}$$

where the values in parentheses are the estimates of the standard errors for the coefficients. The correlation coefficient  $(r^2)$  was 0.63, and the equation predicted the half-life for the individual ponds with an average error of 10 days. The equation correctly predicted a long half-life of 50 days for the two deep ponds in Florida with an average water depth of 5.2 m. However, it failed to predict a long half-life for the relatively shallow ponds in Missouri and Tennessee, thus implying that factors other than water depth are important in predicting the half-life. Deleting the latter two pond trials from the model resulted in the equation

$$t_{1/2} (\text{days}) = 10.5 \text{ WD} - 1.54 (2) (1.31) (2.54)$$

which produces an  $r^2$  value of 0.93 and predicts the half-life with an average error of 5 days.

In an effort to improve the predictive capability of the mathematical model, several physical and chemical variables were used in various combinations for 12 of the pond trials in Table II. This approach identified dissolved oxygen (DO) and water turbidity (T) as variables which improve the prediction of half-life values. This relationship between half-life, turbidity, and dissolved oxygen may

possibly be explained by the effect of these two variables on photolysis rates. The amount of oxygen in aqueous solutions of fluridone has been determined to affect photolysis rates (Saunders and Mosier, 1983). Water turbidity would also be expected to affect photolysis by reducing sunlight penetration.

When the DO and T data for 12 ponds (Table II) were used, the following regression equation was obtained:

$$t_{1/2} \text{ (days)} = 25.3 + 2.36 T - 3.81 \text{ DO} (7.76) (0.56) (1.31)$$
(3)

This model predicted the half-life with an average error of 6 days. Also, this model resulted in improved predictions for the ponds in Tennessee (predicted  $t_{1/2} = 45$  days) and Missouri (predicted  $t_{1/2} = 32$  days). Deleting the latter two ponds from the model resulted in the equation

$$t_{1/2} (\text{days}) = \begin{array}{c} 14.2 + 0.57 \ T - 0.97 \ \text{DO} \\ (5.79) \ (0.55) \ (1.16) \end{array}$$
(4)

which predicted the half-life for the 10 ponds with an average error of only 3 days. The addition of other variables to form a three-parameter equation failed to improve the predictability of half-lives.

The true utility of any mathematical model is its ability to predict an outcome from a limited amount of information. Equations 3 and 4 were constructed from average values of the chemical and physical data obtained from the ponds on the same days that residue samples were collected during the first month after treatment. To test the predictability of these equations, values for dissolved oxygen and turbidity taken a short time (normally 24 h or less) prior to treatment were substituted into the equations to predict the half-life. The predicted and observed values are presented in Table V. Equation 3 resulted in errors of prediction ranging from 1 to 21 days, with an average of 8 days.

When pretreatment values for DO and T in eq 4 (which resulted from removal of the Tennessee and Missouri trials from the model) were used, errors ranged from 1 to 9 days with an average of 5 days. Thus, it appears that eq 4 can be used to predict an approximate half-life of fluridone in many ponds prior to treatment.

Equation 4 was constructed from variables which would be expected to primarily affect the rate of photolysis. However, there are other variables (e.g., aquatic plant uptake, hydrosoil adsorption, and metabolism of fluridone by aquatic organisms) which could also influence the half-life of fluridone. These variables are not as easily obtained from pretreatment observations in the field and,

Table VI. Summary of Fluridone Dissipation Data in Pond and Lake Hydrosoil following Applications of SONAR AS

body of	time after	no. of	fluridone residu	ie, kg/ha
water	treatment	trials	range	av
pond	1 day	13	NDR <sup>a</sup> -0.40	0.04
-	3 days	14	NDR-0.19	0.06
	1 week	14	NDR-0.52	0.11
	2 weeks	16	NDR-0.30	0.11
	1 month	16	NDR-0.56	0.15
	2 months	14	NDR-0.30	0.07
	4 months	16	NDR-0.17	0.04
	6 months	7	NDR-0.12	0.03
	12 months	8	NDR-0.07	0.02
lake	1 day	2	0.01 - 0.02	0.02
	1 week	4	NDR	NDR
	2 weeks	4	NDR-0.02	0.01
	3 weeks	2	NDR	NDR
	1 month	2	NDR	NDR
	2 months	2	NDR	NDR
	3 months	2	NDR	NDR

<sup>a</sup> No detectable residue at a detection limit of approximately 0.01 kg/ha.

Table VII. Summary of Fluridone Dissipation Data in Lake and Pond Hydrosoil following Applications of SONAR 5P

body of	time after	no, of	fluri <b>do</b> ne re kg/ha	sidue,
water	treatment	trials	range	av
pond	1 day	6	NDR <sup>a</sup> -1.15	0.36
-	3 days	6	0.02-0.62	0.29
	1 week	6	NDR-0.54	0.17
	2 weeks	6	0.06 - 1.44	0.55
	3 weeks	3	NDR-0.29	0.12
	1 month	6	0.04-0.46	0.16
	2 months	5	NDR-0.19	0.08
	4 months	6	NDR-0.22	0.07
	6 months	2	NDR-0.18	0.09
	12 months	1	NDR	NDR
lake	1 day	2	0.01-0.06	0.03
	1 week	2	0.02-0.03	0.03
	2 weeks	3	NDR	NDR
	3 weeks	3	NDR	NDR
	1 month	2	NDR	NDR
	2 months	2	NDR-0.02	0.01
	3 months	2	NDR	NDR

<sup>a</sup> No detectable residue at a detection limit of approximately 0.01 kg/ha.

thus, were not included in the mathematical model. It is recognized that the addition of such variables could improve the model considerably if the relationship between half-life values and one or more of these variables is strong.

Accumulation and Dissipation in Hydrosoil. The residue pattern for fluridone in hydrosoil following applications of SONAR AS and SONAR 5P is summarized for all of the field trials in Tables VI and VII, respectively. With SONAR AS, the average adsorption of residues onto hydrosoil reached a maximum of 0.15 kg/ha 1 month after treatment and declined to approximately 10% of the maximum (2% of the application rate) within 1 year. With SONAR 5P, the average residues reached a maximum of 0.55 kg/ha within 14 DAT and then declined at a rate similar to that in the AS trials. The collection of SONAR pellets in the hydrosoil samples probably contributed to the large residues on the first few sampling dates, and the initial rapid decline in residues from the 5P trials was probably the result of the clay pellets dissolving on the hydrosoil surface and releasing fluridone into the water. Residues were not detected in the hydrosoil from SONAR 5P trials 1 year after treatment.

Applications of SONAR to small plots (0.8-4.0 ha) in large lakes resulted in negligible residues in the hydrosoil (Tables VI and VII). These results were likely due to dispersal of fluridone into the surrounding untreated areas of the lakes before significant deposition onto the hydrosoil could occur.

Half-lives for fluridone in the hydrosoil from individual trials could not be reliably estimated due to variable residue patterns observed in several ponds. Residues in hydrosoil were especially variable in the SONAR 5P trials, probably as a result of collecting the clay pellets containing fluridone in some of the hydrosoil samples. However, an average half-life was estimated for the SONAR AS trials from the data in Table VI by calculating an equation for the least-squares line drawn through that portion of the decline curve which approximated a linear rate of dissipation. The least-squares line was described by the equation

kg of fluridone/ha =  $-7.06 \times 10^{-4}$  (days) + 0.141

The equation had a correlation coefficient of 0.86 and resulted in an average half-life estimation of approximately 3 months for fluridone in pond hydrosoil.

Metabolism studies with  $[^{14}C]$ fluridone in water-sediment systems conducted in the laboratory have resulted in the very slow degradation of fluridone (apparently by microorganisms) to a single major metabolite (III). However, the hydrosoil degradate was not detected in watersediment systems maintained outdoors (Rainey and Berard, 1979; Muir and Grift, 1982). Apparently, rapid aqueous photolysis so greatly predominates in natural sunlight that fluridone dissipates from the aquatic environment before the much slower microbial degradation occurs.

The observation that the hydrosoil metabolite (III) does not form under actual field conditions was confirmed in 20 pond trials. Hydrosoil samples were collected at 4–25 months after treatment with each SONAR formulation, and residues of III were not detected in any of the samples. Even in six ponds treated at 1.68 kg/ha (twice the recommended application rate) for 2 consecutive years, no detectable residue of III resulted in the hydrosoil at a detection limit of 0.02–0.05 ppm (approximately 0.01 kg/ha). Thus, it appears that fluridone dissipated from hydrosoil by a mechanism other than degradation to III.

Laboratory adsorption and desorption studies conducted with fluridone in sediment-water systems have demonstrated that fluridone establishes an equilibrium concentration between the water and hydrosoil, and removal of the herbicide from the water results in desorption of the herbicide from the hydrosoil to maintain the equilibrium. Under actual field conditions, fluridone would be expected to dissipate from hydrosoil by gradual desorption into the water, where it would be photodegraded (Lilly Research Laboratories, 1981). As a result, large residues of the herbicide have not persisted or accumulated in hydrosoil following annual applications of SONAR.

**Bioconcentration and Dissipation in Fish.** The accumulation and dissipation patterns for residues in fish are summarized for all of the field trials in Tables VIII-X. The total residue of fluridone plus a single major metabolite (II) are reported for edible, inedible, and whole body tissues. Residues in fish during the first 2-4 weeks after treatment were usually lower in fish from SONAR 5P trials than in those from the AS trials, apparently as a result of the lower initial concentration of fluridone in the water treated with the clay pellets. For SONAR AS (Table VIII), the average total residue was a maximum at 1 DAT in edible tissue (0.132 ppm), 14 DAT in inedible tissue (0.528

Table VIII.	Summary of the	Total Residue of	Fluridone plus	Its Metabolite	(II) in Fish follow	ing Applications
of SONAR A	AS to Ponds					

	total residue, ppm							
time after	edible tissue		inedible ti	ssue	whole bo	whole body		
treatment	range	av	range	av	range	av		
1 day	0.071-0.252	0.132	0.057-0.621	0.354	0.067-0.509	0.291		
3 days	0.022 - 0.137	0.094	0.112 - 0.765	0.444	0.092-0.642	0.353		
1 week	0.008 - 0.216	0.072	0.008-1.385	0.331	0.037-0.965	0.257		
2 weeks	NDR-0.076	0.046	0.139 - 1.067	0.528	0.097-0.798	0.399		
1 month	NDR-0.153	0.053	0.037-0.533	0.239	0.028 - 0.347	0.172		
2 months	NDR-0.062	0.021	0.019 - 0.175	0.095	0.007-0.143	0.072		
4 months	NDR-0.013	$NDR^{a}$	NDR-0.107	0.026	NDR-0.088	0.020		
12 months	NDR	NDR	NDR	NDR	NDR	NDR		

<sup>a</sup> No detectable residue at a detection limit of approximately 0.005-0.010 ppm.

Table IX. Summary of the Total Residue of Fluridone plus Its Metabolite (II) in Fish following Applications of SONAR 5P to Ponds

	total residue, ppm							
time after	edible tiss	edible tissue		ssue	whole bo	dy		
treatment	range	av	range	av	range	av		
1 day	NDR <sup>a</sup> -0.283	0.067	NDR-0.292	0.071	0.005-0.290	0.071		
3 days	NDR-0.045	0.016	0.025 - 0.165	0.089	0.010 - 0.135	0.067		
1 week	NDR-0.073	0.022	0.017 - 0.320	0.173	0.013 - 0.201	0.124		
2 weeks	NDR-0.028	0.019	0.097 - 0.233	0.165	0.064 - 0.170	0.120		
3 weeks	NDR-0.053	0.021	0.054 - 0.409	0.180	0.031 - 0.356	0.143		
1 month	0.018 - 0.054	0.036	0.210 - 0.358	0.268	0.157 - 0.229	0.185		
2 months	0.008-0.039	0.018	0.073 - 0.184	0.122	0.056-0.141	0.092		
4 months	NDR-0.017	0.008	NDR-0.107	0.044	NDR-0.088	0.037		

<sup>a</sup> No detectable residue at a detection limit of approximately 0.005-0.010 ppm.

Table X. Summary of the Total Residue of Fluridone plus Its Metabolite (II) in Fish following Applications of SONAR AS and 5P to Ten-Acre Plots in Lake Pierce, Florida

			total residue	, ppm		
days after treatment	edible tissue		inedible ti	ssue	whole body	
	range	av	range	av	range	av
7 14	NDR <sup>a</sup> -0.020 NDR-0.020	0.007 0.009	NDR-0.138 0.012-0.118	0.049 0.034	NDR-0.093 0.009-0.086	0.036 0.028

<sup>a</sup> No detectable residue at a detection limit of approximately 0.005-0.010 ppm.

Table XI.	Average Bioconcentration	Factor for the Total Residue of	of Fluridone plus Its Metabolit	e (II) in Fish Tissues

		av BCF (total residue)			
fish species	no, of samples	edible	inedible	whole	
bluegill (Lepomis macrochirus)	63	0.94	5.34	4,58	
green sunfish (Lepomis cyanellus)	3	1.61	4.18	1.59	
warmouth sunfish (Chaenobryttus gulosus)	9	1.42	3.52	2.22	
tilapia ( <i>Tilapia</i> sp.)	7	0.96	$\mathbf{N}\mathbf{A}^{a}$	NA	
largemouth bass (Micropterus salmoides)	34	1.23	6.00	4.89	
rainbow trout (Salmo gairdneri)	8	2.30	23.39	15.51	
chub sucker (Erimyzon sucetta)	6	1.45	9.63	5.49	
channel catfish (Ictalurus punctatus)	22	1.92	10.29	8.71	
black bullhead (Ictalurus melas)	10	1.76	8.73	6.98	
brown bullhead (Ictalurus nebulosus)	13	2.46	NA	NA	

<sup>a</sup> Information not available.

ppm), and 14 DAT in whole fish (0.399 ppm). For SONAR 5P (Table IX), the average concentration reached a maximum 1 DAT in edible tissue (0.067 ppm), 28 DAT in inedible tissue (0.268 ppm), and 28 DAT in whole fish (0.185 ppm).

Residues were normally not found in fish after the herbicide had dissipated from the water. The average residues in edible fish tissue and water were both less than 0.01 ppm 4 months after treatment.

Residues in fish from lake trials (Table X) were much lower than those from ponds. The lower residues in fish correspond to the lower concentration of fluridone in the water of lake trials (Tables III and IV).

The tendency of fish to accumulate chemical residues is normally expressed as a bioconcentration factor (BCF), which is defined as the ppm concentration of the residue in fish divided by the ppm concentration in water (Kenaga, 1972). BCFs for fluridone were calculated by using the concentrations in fish and water on each sampling date. BCFs for the fish metabolite (II) were also calculated by converting residues of II to the fluridone molecular weight equivalent.

The average BCF for the total residue of fluridone plus II in the edible, inedible, and whole body tissues of 10 fish

Table XII. Average Bioconcentration Factors for Fluridone, Its Metabolite (II), and the Total Residue in Ten Fish Species from Field Trials

chemical residue	av BCF <sup>a</sup>			
	edible	inedible	whole	
fluridone	1.20	3.14	3.01	
metabolite (II)	0.23	4.16	3.07	
total	1.33	7.38	6.08	

 $^a$  Average bioconcentration factor determined from 175 samples.

species collected from the field trials is summarized in Table XI. The BCF was very low in all fish species, indicating that large residues will not accumulate in fish as a result of SONAR applications.

The average BCF for fluridone, the metabolite, and the total residue in all fish species combined is summarized in Table XII. The average BCFs for the total residue were 1.33, 7.38, and 6.08 in edible, inedible, and whole fish tissues, respectively. The edible tissue bioconcentrated fluridone 5.2 times greater than the metabolite. However, the BCF for the inedible tissue was 1.3 times higher for the metabolite, and the BCF for whole fish was nearly identical for both compounds.

The observed BCFs for fluridone correlate well with its low *n*-octanol/water partition coefficient. The log  $K_{\rm ow}$  for fluridone was determined to be 1.87 (Lilly Research Laboratories, 1981) by using established procedures (Environmental Protection Agency, 1975). An equation relating BCFs of chemicals in whole fish to partition coefficients (Veith et al., 1979) predicts a BCF of 7.8 for fluridone. Thus, applications of SONAR to lakes and ponds would not be expected to result in a large buildup of residues in the aquatic food chain.

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#### LITERATURE CITED

- Arnold, W. R. J. Aquat. Plant Manage. 1979, 17, 30.
- Environmental Protection Agency Fed. Regist. 1975, 40, 26880. Grant, D. L.; Warner, L. C.; Arnold, W. R.; West, S. D. Proc.,
- South. Weed Sci. Soc. 1979, 32, 293.
- Kenaga, E. E. In "Environmental Toxicology of Pesticides"; Matsummura, F.; Bousch, M. G.; Misato, T., Eds.; Academic Press: New York, 1972.
- Lilly Research Laboratories "SONAR Technical Manual"; Lilly Research Laboratories: Greenfield, IN, 1981.
- Marquis, L. Y.; Comes, R. D.; Yang, C. P. Pestic. Biochem. Physiol. 1982, 17, 68.
- McCowen, M. C.; Young, C. L.; West, S. D.; Parka, S. J.; Arnold, W. R. J. Aquat. Plant Manage. 1979, 17, 27.
- Muir, D. C. G.; Grift, N. P. J. Agric. Food Chem. 1982, 30, 238.
- Muir, D. C. G.; Grift, N. P.; Blouw, A. P.; Lockhart, W. L. J. Environ. Qual. 1980, 9, 151.
- Parka, S. J.; Arnold, W. R.; McCowen, M. C.; Young, C. L. Proc. EWRS Symp. Aquat. Weeds, 5th 1978.
- Rainey, D. P.; Berard, D. F., Lilly Research Laboratories, personal communication, 1979.
- Rivera, C. M.; West, S. D.; Perez, J. Proc. Annu. West. Soc. Weed Sci., 32nd 1979, 32, 67.
- Sanders, D. R.; Theriot, R. F.; Arnold, W. R.; West, S. D. U.S. Army Engineer Waterways Experiment Station Technical Report A-79-3, 1979.
- Saunders, D. G.; Mosier, J. W. J. Agric. Food Chem. 1983, 31, 237.
- Veith, G. D.; DeFoe, D. L.; Bergstedt, B. V. J. Fish. Res. Board Can. 1979, 36, 1040.
- West, S. D. J. Agric. Food Chem. 1978, 26, 664.
- West, S. D., submitted for publication in Anal. Methods Pestic. Plant Growth Regul., 1983.
- West, S. D.; Burger, R. O. J. Assoc. Off. Anal. Chem. 1980, 63, 1304.
- West, S. D.; Day, E. W.; Burger, R. O. J. Agric. Food Chem. 1979, 27, 1066.
- West, S. D.; Parka, S. J. J. Agric. Food Chem. 1981, 29, 223.

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# Metabolism of p-Chlorobenzotrifluoride by Rats

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When rats were given a single oral dose of p-chloro[trifluoromethyl-<sup>14</sup>C]benzotrifluoride at 1 mg/kg, 3-4 and 14-15% of the applied <sup>14</sup>C were excreted in feces and urine, respectively. The major urinary metabolites were glucuronides of dihydroxybenzotrifluoride and 4-chloro-3-hydroxybenzotrifluoride (each representing 3-4% of the applied <sup>14</sup>C), as well as minor amounts of a mercapturic acid conjugate of p-chlorobenzotrifluoride. p-Chlorobenzotrifluoride itself was rapidly expired by rats (62-82% of the applied dose) and was the major <sup>14</sup>C-labeled residue in feces. In general, levels of <sup>14</sup>C-labeled residues in tissues were low, but the small amount of radiolabel in the rat carcass 4 days after dosage (ca. 1% applied dose) was also identified as p-chlorobenzotrifluoride and was found predominantly in fat.

p-Chlorobenzotrifluoride (p-chloroBTF, 1) is an important intermediate in the synthesis of certain crop

protection chemicals, especially herbicides (Boudakian, 1980), thereby offering a significant potential for occupational exposure. The metabolic fate of this compound is unreported although Cacco and Ferrari (1982) communicated the absorption and translocation of p-chloroBTF in soil and crops. We now report the metabolic fate of p-

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