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Dissipation of the Experimental Aquatic Herbicide Fluridone from Lakes and Ponds

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The dissipation of the aquatic herbicide fluridone, 1-methyl-3-phenyl-5-[3-trifluoromethyl)phenyl]-4(1*H*)-pyridinone, has been determined in experiments conducted in small ponds at three different geographic regions in the United States and in Gatun Lake of the Panama Canal. Fluridone dissipated rapidly from the water, with a half-life averaging 5 days. The dissipation was due in part to deposition on hydrosoil and uptake by aquatic plants, although evidence is presented to suggest photolysis as a contributing mechanism. The accumulation and dissipation patterns of fluridone on hydrosoil were highly variable. The herbicide demonstrated a very low potential for bioconcentration in fish, zooplankton, and aquatic plants.

Fluridone, 1-methyl-3-phenyl-5-[3-(trifluoromethyl)-phenyl]-4(1*H*)-pyridinone, is an experimental herbicide currently being developed by Elanco Products Co., a Division of Eli Lilly and Co. Fluridone has demonstrated potential as both a terrestrial herbicide for use on cotton (Waldrep and Taylor, 1976, 1977; Webster et al., 1977) and as an aquatic herbicide with unique activity against aquatic vascular plants at low application rates (McCowen at al., 1979; Sanders et al., 1979; Arnold, 1979; Parka et al., 1978).

The absorption, translocation, and metabolism of fluridone in several agronomic crops has been reported (Berard et al., 1978), and mode of action studies have been published (Bartels and Watson, 1978; Devlin et al., 1978; Berard et al., 1978). The dissipation of fluridone when applied as an aquatic herbicide to a Canadian pond has also been reported (Muir and Grift, 1978). In the Canadian study, fluridone exhibited a half-life of 4–7 days in the water and greater than 3 months in the hydrosoil. In the same study duckweed (*Lemna minor*) was reported to concentrate the herbicide by a factor of 85 compared to the concentration in the water, although this amount was estimated to represent less than 1% of the total amount of herbicide applied to the pond (Muir and Grift, 1978).

In this paper the dissipation of fluridone from water and hydrosoil is reported for studies conducted in small ponds located in Michigan, New York, and Florida and in Gatun Lake of the Panama Canal. The residue level of fluridone in fish, zooplankton, and aquatic plants is also reported for some of the small pond experiments.

EXPERIMENTAL SECTION

Methods of Application and Plot Description. The initial study with fluridone was conducted at Lake City, Michigan, in June, 1976 (McCowen et al., 1979). The pond was 0.04 ha in size with an average depth of 1.1 m. Fluridone formulated as a 4 lb/per gallon aqueous suspension (4AS) was subsurface applied (SSA) with a conventional CO_2 sprayer at a rate of 0.1 ppm relative to the total water column, which was equivalent to 1.12 kg/ha.

A second trial was begun at Ithaca, New York, in May, 1977 (McCowen et al., 1979). The ponds in this experiment were 0.07 ha in size with an average depth of 0.9 m. Fluridone 4AS was applied either by SSA or by layering the herbicide on the bottom of the pond with a hand-held CO_2 sprayer. With the SSA technique, fluridone was applied at 0.3 ppm relative to the total water column, which was equivalent to 2.7 kg/ha. With the layered technique, fluridone was applied at 0.3 ppm relative to the bottom one-third of the water column, which was equivalent to 0.9 kg/ha.

A third trial was begun in April, 1977, at Orlando, Florida, with a 0.16-ha pond averaging 0.7 m deep (Arnold, 1977). Fluridone 4AS was applied at 0.3 ppm relative to the total water column, which was equivalent to 2.0 kg/ha.

A fourth trial was begun at Hialeah, Florida, in September, 1977, with 0.4-ha and 0.8-ha ponds averaging 5.2 m deep (Arnold, 1979). The herbicide was applied to the bottom of the ponds via an airboat equipped with a two-stage piston pump and weighted, trailing hoses. The application rates were 1.1 and 1.7 kg/ha, which were equivalent to 0.02 and 0.03 ppm relative to the total water column.

Several trials were begun in January, 1978, in selected areas of Gatun Lake, a man-made reservoir in the Panama Canal (Sanders et al., 1979). Fluridone 4AS was applied below the water surface from an airboat equipped with a conventional spray pump and weighted, trailing hoses 6.1 m long. Fluridone formulated as a 5% pellet (5P) was surface applied (SA) using a rotary spreader mounted on the front of an airboat. The pellets sank to the hydrosoil. Both formulations were applied at 1.7 and 6.7 kg/ha to plots which varied in size from 0.7 to 1.0 ha and in depth from 2.1 to 8.2 m.

Residue Sampling Procedures. Residue samples were collected for analysis at regular intervals following the application of fluridone. In the Michigan trial, water samples were collected just below the water surface. In the other experiments, samples were collected at various depths on each sampling date. Water samples were preserved with 0.5 mL of concentrated sulfuric acid per liter and stored at 4°C until analyzed. (Previous studies had established the stability of fluridone under these conditions.)

Three to ten hydrosoil subsamples were collected with a soil sampler containing removable 2.54 cm i.d. plastic tubes. These cores were taken at depths of 0–7.6 to 0–25.4 cm, depending on the texture and hardness of the hydrosoil. Upon receipt, hydrosoil subsamples from individual tubes were combined and excess water was removed

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by filtration. After the soil was air-dried for 2–3 days, it was ground, blended, weighed, and stored at 4 °C until analyzed. All analytical results for hydrosoil were subsequently calculated on a dry weight basis.

Fish were collected by rod and reel from two of the ponds. The species included green sunfish (*Lepomis cyanellus*), pumpkinseed sunfish (*Lepomis gibbosis*), bluegill (*Lepomis macrochirus*), redear sunfish (*Lepomis microlophus*), largemouth bass (*Micropterus salmoides*), and black bullhead (*Ictalurus melas*). All fish samples were frozen for shipment to the analytical laboratory, where they were sliced and blended to form homogeneous samples which were then stored in a freezer until analyzed.

In the Michigan experiment, zooplankton was collected with a submerged light trap. The samples were then frozen until analyzed.

Several species of vascular aquatic weeds were also collected from the ponds. The predominant species included *Hydrilla verticillata*, *Elodea canadensis*, and *Potamogeton amplifolius*. The plants were frozen for shipment to the analytical laboratory, where they were frozen with liquid nitrogen, finely ground, and stored in a freezer.

Residue Analysis. Complete details of the analytical procedures used for determining fluridone residues have been discussed in a previous publication (West, 1978). Briefly, fluridone was extracted from water with dichloromethane, from hydrosoil with 2 N NaOH/methanol (1:1), and from fish, plants, and zooplankton with methanol. The methanolic extracts were combined with 5% saline solution, washed with hexane, and then extracted with dichloromethane. The dichloromethane extracts were evaporated and the fluridone residues were reacted with phosphorus tribromide to form a brominated derivative. Following purification by alumina column chromatography, the brominated derivative was measured by electron-capture gas chromatography. The gas chromatograph was a Hewlett-Packard Model 402 equipped with a ^{63}Ni electron-capture detector. The column was a 180 cm × 0.3 cm i.d. borosilicate glass tube containing 2% OV-17 on 80/100 mesh Chromosorb W-HP. The oven, detector, and injection block were maintained at 195, 290, and 230 °C, respectively.

Aqueous Photolysis Study. An aqueous photolysis study was conducted in a light box containing four Westinghouse FS20 sunlamps and four GE F20T12BL black lights. This combination yielded an average light intensity of approximately 2000 $\mu W/cm^2$ as measured by a YSI Model 65 radiometer. Quartz flasks containing aqueous solutions of analytical grade fluridone were adjusted to pH 7.0 and were placed in the light box on a rotating turntable. Aliquots of the exposure solution were periodically removed and extracted with chloroform. Following concentration of the extracts, underivatized fluridone was measured with a Hewlett-Packard Model 402 gas chromatograph equipped with a flame ionization detector. The column was a 120 cm × 0.3 cm glass column packed with 3% Apiezon L on 80/100 mesh Chromosorb W-HP. The following temperatures were maintained isothermally: oven (265 °C), flash heater (280 °C), and detector (290 °C). Nitrogen was the carrier gas at a flow rate of 40 mL/min. Under these conditions, fluridone exhibited a retention time of 5 min and a peak height of 9.0 cm for an injection of 50 μg.

RESULTS AND DISCUSSION

Recoveries and Test Sensitivities. Recovery efficiencies were determined by fortifying an untreated sample with fluridone and processing the fortified sample with each set of residue samples. The recovery data are summarized in Table I, and representative chromatograms demonstrating the recovery of fluridone from water and fish are contained in Figures 1 and 2. The detection limits for fluridone were approximately 0.001 ppm in water, 0.01–0.02 ppm in zooplankton, and 0.01 ppm in hydrosoil, fish, and aquatic plants.

Table I. Summary of Fluridone Recovery Efficiencies

sample type	ppm fortified	no. of recov.	% recovery range	% recovery av
water	0.001	2	80–80	80
	0.004	4	57–114	92
	0.008	4	87–135	102
	0.010	17	59–119	88
	0.020	2	104–116	110
	0.050	2	83–97	90
	0.100	1	80	80
	0.125	4	40–98	80
hydrosoil	0.030	6	39–89	70
	0.060	9	60–167	98
	0.100	2	81–83	82
	0.200	6	63–87	71
fish	0.020	7	71–121	89
	0.100	2	79–101	90
	0.200	8	62–104	82
zooplankton	0.020	2	51–82	67
	0.100	2	75–92	84
plants	0.020	2	91–97	94
	0.050	2	74–112	93
	0.200	8	54–122	88

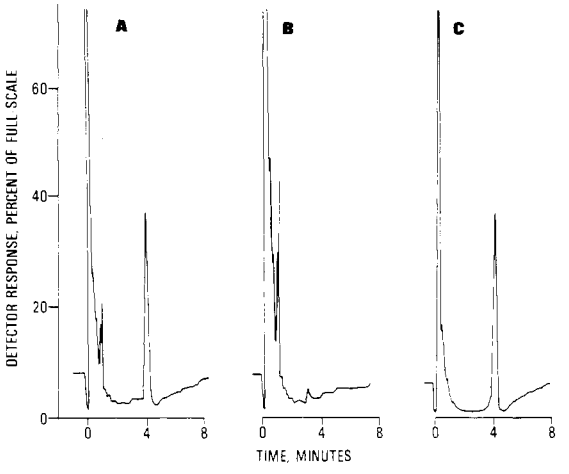

Figure 1. Gas–liquid chromatograms demonstrating the recovery of fluridone from pond water: (A) brominated fluridone standard, equivalent to 0.38 ng of fluridone; (B) pond water extract (untreated control); (C) pond water extract (recovery, 0.01 ppm), equivalent to 97% recovery.

Dissipation of Fluridone from Water. In the Michigan trial (Table II) a single composite water sample was analyzed for each sampling date. In the remaining experiments, samples collected from various depths were analyzed separately to observe gradients in concentration which might be present. Although concentration gradients were sometimes observed on a few of the initial sampling dates, sampling at various depths normally did not demonstrate well-defined gradients. Consequently, the water residue data presented in Tables III–VIII are averages of the individual values on a given sampling date.

The rate of fluridone dissipation from the water in each experiment was determined by plotting the percent of the herbicide remaining vs. the number of days after treatment. The percent of fluridone remaining was normally

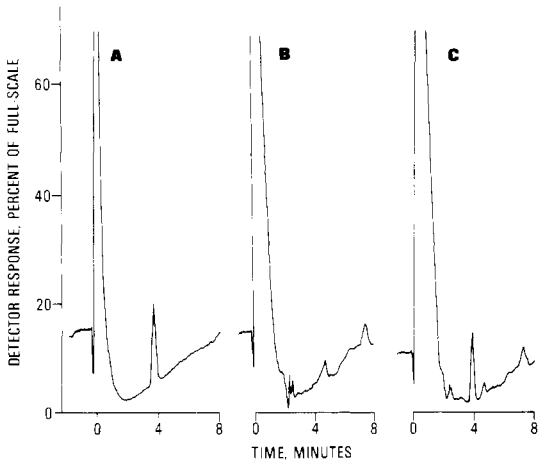

Figure 2. Gas–liquid chromatograms demonstrating the recovery of fluridone from fish: (A) brominated fluridone standard, equivalent to 0.11 ng of fluridone; (B) fish extract (untreated control); (C) fish extract (recovery, 0.02 ppm), equivalent to an 85% recovery.

Table II. Fluridone Residues following Subsurface Application of Fluridone 4AS at 1.12 kg/ha to a Pond in Michigan

	fluridone residues, ppm			
DAT[a]	water	fish	zooplankton	plants[b]
1	0.090	0.054[c] 0.023[c]	0.115	0.440
7	0.021	0.023[d] 0.019[e]	0.032	0.300
14	0.006	0.010[f] 0.010[f]	NDR[g]	0.093
27	0.002	NDR[d] NDR[e]	0.020	0.018
54	NDR	NDR[d] NDR[e] NDR[f]	NDR	0.009
83	NDR	NDR[d] NDR[e]	NDR	NDR
110	NDR	NDR[c] NDR[e]	NDR	NDR

[a] Days after treatment. [b] Predominantly *Potamogeton amplifolius*. [c] Green sunfish (*Lepomis cyanellus*). [d] Pumpkinseed sunfish (*Lepomis gibbosis*). [e] Largemouth bass (*Micropterus salmoides*). [f] Black bullhead (*Ictalurus melas*). [g] No detectable residue.

Table III. Fluridone Residues following Subsurface Application of Fluridone 4AS at 2.7 kg/ha to a Pond in New York

	fluridone residues		
DAT[a]	water, ppm	hydrosoil, kg/ha	plants,[b] ppm
1	0.303		
3	0.265	0.024	0.33
7	0.187	0.008	3.98
14	0.131	0.124	2.32
28	0.041	0.442	2.05
84	0.045	0.075	0.20
112	0.015	0.085	0.12

[a] Days after treatment. [b] Predominantly *Elodea canadensis*.

based upon the initial concentration in the water, except when the maximum concentration was not observed on the initial sampling date due to uneven dispersal of the herbicide. In the latter case, the half-life calculations were based upon the length of time required for dissipation to 50% of the maximum concentration.

Table IV. Fluridone Residues following Application of Fluridone 4AS at 0.9 kg/ha to the Bottom of a Pond in New York

	fluridone residues		
DAT[a]	water, ppm	hydrosoil, kg/ha	plants,[b] ppm
1	0.109		
3	0.064	0.015	0.271
7	0.103	0.008	0.467
14	0.032	0.030	0.416
28	0.027	0.063	0.285
84	0.023	0.082	
112	0.011	0.092	0.220

[a] Days after treatment. [b] Predominantly *Elodea canadensis*.

Table V. Fluridone Residues following Surface Application of Fluridone 4AS at 2.0 kg/ha to a Pond in Orlando, Florida

	fluridone residues	
DAT[a]	water, ppm	hydrosoil, kg/ha
0	0.393	0.150
1	0.197	
7	0.111	0.224
14	0.063	0.162
21	0.053	0.329
28	0.044	0.144
55	0.014	0.121
83	NDR[b]	0.159
364	NDR	0.356

[a] Days after treatment. [b] No detectable residue.

Table VI. Fluridone Residues following Application of Fluridone 4AS at 1.1 kg/ha to the Bottom of a Pond in Hialeah, Florida

	fluridone residues			
DAT[a]	water, ppm	hydrosoil, kg/ha	fish, ppm	plants,[b] ppm
3	0.041	0.104	NDR[d]	0.279
8	0.053	0.072	NDR[d]	0.134
15	0.025	0.125	0.023[d]	0.184
29	0.016	0.297	0.027[d]	0.272
58	0.021	0.277	NDR[d]	
82	0.010	0.198	NDR[d]	0.228
120	0.010	0.118	NDR[d]	0.223
189	0.003	0.071	NDR[d]	0.095
272	0.004	0.056	NDR[d] NDR[e]	0.095
364	NDR[c]	NDR	NDR[d] NDR[f]	NDR

[a] Days after treatment. [b] Predominantly *Hydrilla verticillata*. [c] No detectable residue. [d] Bluegill (*Lepomis macrochirus*). [e] Redear sunfish (*Lepomis microlophus*). [f] Black bullhead (*Ictalurus melas*).

A representative decline curve is shown in Figure 3, and the resulting half-life data are summarized in Table IX. In these trials fluridone exhibited a half-life in the water ranging from 1 to 11 days with an average of 5 days. Furthermore, the rate of dissipation in the Gatun Lake experiment was similar for both the 5P and 4AS formulations. However, in the latter experiment, the presence of small amounts of fluridone in the water from untreated areas of the lake suggested that the dissipation may have been due in part to movement of the herbicide out of the treated area (Table VIII).

Residues of Fluridone on Hydrosoil. The hydrosoil residue data summarized in Tables III–VIII are expressed in terms of kilograms/hectare in order to relate the residue

Table VII. Fluridone Residues following Application of Fluridone 4AS at 1.7 kg/ha to the Bottom of a Pond in Hialeah, Florida

DAT[a]	fluridone residue: water, ppm	hydrosoil, kg/ha	fish, ppm
3	0.053	0.080	NDR[c]
8	0.082	0.123	NDR[c]
15	0.030	0.306	0.023[c]
29	0.036	0.143	NDR[c]
58	0.046	0.307	NDR[c]
82	0.014	0.077	NDR[c]
120	0.011	0.034	NDR[c]
189	0.011	0.119	NDR[c]
272	0.006	0.056	NDR[c]
			NDR[d]
364	0.003	NDR	NDR[c]
			NDR[e]

[a] Days after treatment. [b] No detectable residue. [c] Bluegill (*Lepomis macrochirus*). [d] Redear sunfish (*Lepomis microlophus*). [e] Black bullhead (*Ictalurus melas*).

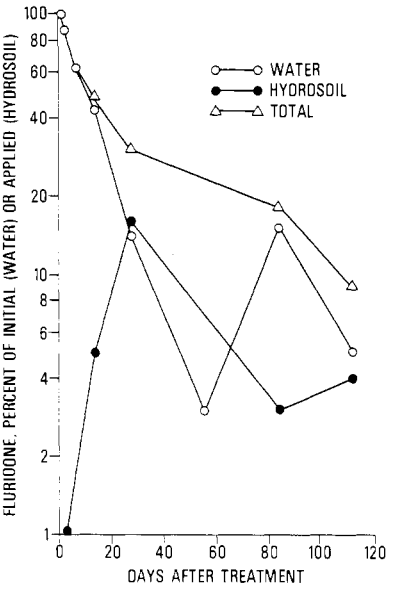

Figure 3. Individual and combined rates of fluridone dissipation from water and hydrosoil in a small pond at Ithaca, New York, treated with fluridone 4AS at 2.7 kg/ha.

levels to the application rates. Residues were converted from ppm to kilograms/hectare according to the following equation:

$$\text{residue (kg/ha)} = (\text{ppm} \times W)/(nr^2 \times 31.8)$$

where W equals the total dry weight (grams) of soil collected, n equals the number of soil subsample cores collected, and r equals the radius (cm) of the soil sampler probe. The conversion factor, 31.8, converts the amount of fluridone from micrograms to kilograms and the total surface area of hydrosoil sampled from cubic centimeters to hectares.

The data show an initial deposition of fluridone onto the hydrosoil and varying patterns of accumulation and dissipation thereafter. In the trial at New York at the 2.7 kg/ha rate (Table III), the residue in the soil gradually increased to a maximum of 0.442 kg/ha at 28 days after treatment. This level was equivalent to 16% of the total amount of fluridone theoretically applied to the pond. The residue level decreased to 0.085 kg/ha (3% of the applied compound) after 112 days.

Residues in the hydrosoil of the second pond at New York (Table IV) increased steadily to a level equivalent to 10% of the applied compound at 112 days after treatment. In the trial at Orlando, Florida (Table V), 18% of the applied herbicide could be accounted for in the hydrosoil after 364 days.

Fluridone residues in the hydrosoil of the first pond at Hialeah, Florida (Table VI), gradually increased to 27% of the applied compound at 29 days after treatment and steadily declined to a nondetectable level after 364 days. A similar pattern was observed in the second pond at Hialeah (Table VII).

In the Gatun Lake experiment (Table VIII), fluridone was not detected in the majority of hydrosoil samples from plots treated with the 4AS formulation. With the 5P formulation, fluridone residues ranged from a nondetectable level to 1.75 kg/ha.

The fluctuating pattern of hydrosoil residues was probably influenced by several factors. Adsorption coefficients determined in the laboratory with terrestrial soils have ranged from a value of 3 on sand to 16 on a loam soil (Loh and Buchanan, 1978). Fluridone was thus ex-

Table VIII. Fluridone Residues following Application of Fluridone 4AS and 5P to Gatun Lake in the Panama Canal

formulation	rate, kg/ha	sample	fluridone residues: 1 DAT[a]	7 DAT	14 DAT	21 DAT	28 DAT	56 DAT	84 DAT
4AS	1.7	water (ppm)	0.039	0.012	0.003	0.001	NDR[b]	NDR	0.005
		hydrosoil, kg/ha	0.02	NDR	0.02	NDR	NDR	NDR	NDR
4AS	1.7	water (ppm)	0.012	0.004	0.006	NDR	0.001	NDR	NDR
		hydrosoil, kg/ha	0.01	NDR	NDR	NDR	NDR	NDR	NDR
4AS	6.7	water, ppm	0.046	0.015	0.004	NDR	0.002	NDR	NDR
		hydrosoil, kg/ha	0.01	NDR	NDR	NDR	NDR	NDR	NDR
4AS	6.7	water, ppm	0.036	0.004	0.003	NDR	0.001	NDR	NDR
		hydrosoil, kg/ha	0.03	0.02	NDR	NDR	NDR	NDR	NDR
5P	1.7	water, ppm	0.032	0.006	0.002	0.003	0.002	NDR	NDR
		hydrosoil, kg/ha	0.01	0.03	NDR	NDR	0.02	NDR	NDR
5P	1.7	water, ppm	0.011	0.005	0.004	0.001	NDR	NDR	NDR
		hydrosoil, kg/ha	0.06	0.02	NDR	NDR	NDR	NDR	NDR
5P	6.7	water, ppm	0.029	0.011	0.004	0.002	0.002	NDR	NDR
		hydrosoil, kg/ha	1.75	1.08	0.04	NDR	0.16	0.07	0.08
5P	6.7	water, ppm	0.027	0.010	0.006	0.001	0.002	NDR	NDR
		hydrosoil, kg/ha	0.13	NDR	0.02	NDR	NDR	1.01	0.07
control	0.0	water, ppm	0.014	0.008	0.004	NDR	0.002	NDR	NDR
		hydrosoil, kg/ha	NDR	NDR	NDR	NDR	NDR	NDR	NDR
control	0.0	water, ppm	0.006	0.009	0.002	NDR	NDR	NDR	NDR
		hydrosoil, kg/ha	NDR	0.02	NDR	NDR	NDR	NDR	NDR

[a] Days after treatment. [b] No detectable residue.

Table IX. Fluridone Half-Lives in Water and Combined Half-Lives in Water and Hydrosoil

location	formulation	rate, kg/ha	half-lives, days: water	half-lives, days: combined (water and soil)
Lake City, MI	4AS	1.1	4	N/A[a]
Ithaca, NY	4AS	0.9	11	11
Ithaca, NY	4AS	2.7	11	13
Orlando, FL	4AS	2.0	1	1
Hialeah, FL	4AS	1.1	6[b]	15
Hialeah, FL	4AS	1.7	6[b]	6
Gatun Lake	4AS	1.7	4	4
Gatun Lake	4AS	1.7	4	4
Gatun Lake	4AS	6.7	4	4
Gatun Lake	4AS	6.7	2	2
Gatun Lake	5P	1.7	3	4
Gatun Lake	5P	1.7	5	5
Gatun Lake	5P	6.7	4	6
Gatun Lake	5P	6.7	4	4

[a] Information not available. [b] Half-life calculation based upon percent of maximum concentration observed rather than percent of initial concentration due to uneven dispersal of the fluridone 4AS on the initial sampling date.

pected to favor adsorption onto hydrosoil sediment from the water. This adsorption process should have continued as long as the herbicide remained in the water. In addition, the herbicide was absorbed by aquatic plants, resulting in chlorosis of new growth and a slow vegetative decline. Hence, fluridone released from the decomposing plant material may have contributed to increased residues in the sediment for several weeks following treatment. With the 5P formulation, the random inclusion or exclusion of the formulated pellets in the collected samples may have contributed to the extreme fluctuations in soil residues for the 6.7 kg/ha rate (Table VIII). Other factors which could possibly have contributed to the fluctuating residue patterns include water temperature, volume of water in the pond, and the amount of organic matter in the sediment.

Bioconcentration of Fluridone in Fish. In Michigan, a variety of fish was analyzed whole, with the resulting data being presented in Table II. Fish were also collected from two ponds at Hialeah, Florida, and the analytical results for the body (edible) portion are included in Tables VI and VII.

In the Michigan experiment, a maximum fluridone residue of 0.054 ppm was observed in fish 1 day after treatment (DAT) and steadily declined to a nondetectable level after 14 days. The bioconcentration factor (determined as the ppm concentration in fish divided by the ppm concentration of fluridone in the water) ranged from 0 to 1.7 for the fish from this pond.

In the trials at Hialeah, Florida (Tables VI and VII), fluridone residues were detected in the edible portions of fish only at 15–29 DAT. The herbicide residues ranged from a nondetectable level to 0.027 ppm, and the bioconcentration factor ranged from 0 to 1.7. As a general rule, fluridone was not detected in fish when it was no longer detected in the water.

Bioconcentration of Fluridone in Zooplankton. Fluridone residues were determined in zooplankton from the pond in Michigan, and the data are summarized in Table II. A maximum residue of 0.115 ppm was observed 1 DAT, and the fluridone concentration steadily declined to a nondectable level after 27 days. The bioconcentration factor ranged from 0 to 10, and fluridone was not detected in the zooplankton when it was no longer detected in the water.

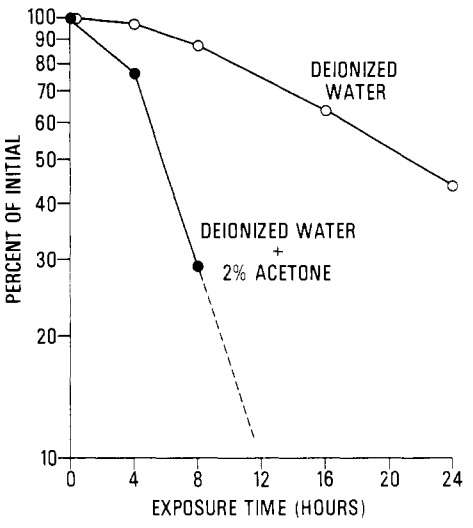

Figure 4. Photolysis of fluridone in deionized water and deionized water containing 2% acetone.

Bioconcentration of Fluridone in Aquatic Plants. Fluridone residues were determined in vascular aquatic plants (consisting primarily of *Potamogeton Amplifolius*) from the pond in Michigan, and the data are summarized in Table II. The fluridone concentration in the plants decreased from a maximum of 0.440 ppm at 1 DAT to a nondectable level at 83 DAT. The bioconcentration factor ranged from 0 to 15.5, with the maximum value occurring 14 DAT.

Aquatic plants (predominantly *Elodea canadensis*) from the New York ponds were also analyzed (Tables III and IV). In both ponds, the maximum residue was observed at 7 days after treatment and declined thereafter. The bioconcentration factor for fluridone in these plants ranged from 1.2 to 50.0. *Hydrilla verticillata* from one of the Florida ponds contained a maximum fluridone residue of 0.279 ppm at 1 day after treatment (Table VI). The residue declined to a nondetectable level after 364 days and the bioconcentration factor ranged from 0 to 31.7.

Overall Dissipation. To accurately determine the overall dissipation of fluridone from the treated lake and ponds would require a knowledge of the total mass of biological matter and the amounts of fluridone present in each component. Lacking this information, estimations were made for the combined rate of fluridone dissipation from soil and water, exclusive of the amounts which might be present in aquatic plant and animal life. To accomplish this, the percent of fluridone remaining in the water on a given date was added to the percent of theoretically applied fluridone which could be accounted for in the hydrosoil on that date. The sum of these percentages was then plotted vs. time, as shown in Figure 3 for one of the ponds in New York. The resulting plot yielded a curve representing the combined dissipation of fluridone from the water and hydrosoil. Half-life data determined in this manner are summarized for each experiment in Table IX.

The combined half-life values ranged from 1 to 15 days with an average of 6 days. The half-lives were similar for both the 5P and 4AS formulations in Gatun Lake, but otherwise varied according to geographic location. The combined half-life values averaged 12 days in New York, 7 days in Florida, and 4 days in Panama. These data suggest that temperature and/or light intensity may be among the factors influencing the dissipation of fluridone.

Laboratory studies conducted in a light box have indicated that fluridone is moderately photolabile in aqueous solution. As shown in Figure 4, fluridone exhibited a

half-life of about 23 h in deionized water and about 6 h in deionized water containing 2% acetone as a triplet sensitizer. Photolysis, especially in the presence of natural sensitizers in lakes or ponds, may thus be an important factor influencing the dissipation of fluridone from aquatic environments.

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Identification of Nitrohexane in Corn Treated with Nitrous Acid

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Nitrohexane has been identified as a major product following deliberate nitrosation of corn. Identification was based on chromatographic and mass spectral data. This finding is discussed in relation to the high incidence of stomach cancer in a region of southern Colombia. We also show that nitroalkanes give a positive response in the thermal energy analyzer, a device which is used as a specific detector for *N*-nitroso compounds.

The occurrence of nitrosamines in nitrite-treated meat products has been widely investigated (Scanlan, 1975; Gough et al., 1977). Nitrosamines have been shown to form from secondary amines and nitrite in human gastric juice (Sander, 1967; Sen et al., 1969; Lane and Bailey, 1973) and in the stomachs of animals (Sander et al., 1968; Sen et al., 1969; Alam et al., 1971; Mysliwy et al., 1974). The possibility of gastric nitrosation has assumed an increased importance in view of recent findings of constant, and sometimes high, levels of nitrite in human saliva (Tannenbaum et al., 1974, 1976; Spiegelhalder et al., 1976). However, little work has been done on the determination of compounds that form by deliberate nitrosation of food material as an indication of the kinds of compounds that may form in the gastric environment.

We chose to initiate our research in this area by investigating the nitrosation of corn. There were two reasons for this choice. First, nitrosamine formation from foods of plant origin has not received much attention. Secondly, we are attempting to determine environmental factors related to the high incidence of stomach cancer in a region of southern Colombia (Correa et al., 1975; Cuello et al., 1976). We have already shown a higher average intake of nitrate in the population at risk compared to control populations (Cuello et al., 1976; Tannenbaum et al., 1979). Consumption of corn also has a positive association with risk for stomach cancer in this region (Haenszel et al., 1976).

In this study, corn samples obtained locally and from the high risk area in Colombia were reacted with nitrite under acidic conditions and we have determined the structure of a principal product.

EXPERIMENTAL SECTION

Materials. Yellow corn was obtained from a region of Nariño in Colombia which has a high incidence of gastric cancer. Whole yellow corn from a local (Cambridge, MA) natural foods store and an enriched, degerminated, commercial corn meal were used for comparison. All solvents were either pesticide grade (Mallinckrodt, St. Louis, MO) or high-pressure LC grade (Fisher, Pittsburgh, PA). 1-Nitrohexane was purchased from ICN (Plainsview, NY). Hexyl nitrite was synthesized from 1-hexanol and sodium nitrite (Vogel, 1948).

Analytical Methods. All gas chromatographic procedures used a 2 m × 2.1 mm (i.d.) stainless steel column packed with 3% OV-17 on Chromosorb G-HP (100–120 mesh), at 120 °C (100 °C for amine analysis). Gas chromatography–thermal energy analysis (GC–TEA) was performed as described by Fine and Rounbehler (1975). The TEA pyrolysis oven temperature was 350 °C and the trap was cooled with acetone/dry ice. GC–mass spectrometry was performed on a Hitachi-Perkin Elmer RMU-6 instrument; GC–chemical ionization mass spec-

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