

Potential Formation of N-Methylformamide (NMF) from Fluridone in New England

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INTRODUCTION

Fluridone (1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone) is a herbicide that was registered by the U.S. EPA in 1986 to control a variety of aquatic weeds. This herbicide was extensively tested prior to registration (West et al. 1983), however, concern has arisen over the possible formation of NMF (N-methylformamide), a potential metabolite, in colder, northern waters (William 1987).

NMF is a well-studied chemical that is suspected of being toxic to humans (Kennedy 1986) and was detected as a photolytic breakdown product of fluridone in laboratory experiments in aquaria without aquatic plants or aquatic sediments (Saunders and Mosier 1983). Two subsequent studies conducted in the southern U.S. (Osborne et al. 1989, West et al. 1990), however, failed to detect NMF when fluridone was applied outdoors in natural ponds.

The purpose of this study was to determine if NMF is formed during the degradation of fluridone under natural field conditions in New England. To make this study as conclusive as possible, fluridone was applied at application rates calculated to produce a theoretical concentration of 150 ppb, which is the maximum allowable concentration in potable water.

METHODS

Three ponds in southeastern Massachusetts, two treatment ponds and one control pond, were selected for the study. The experimental ponds constitute "natural" sites, since these ponds were being treated with fluridone for aquatic weed growth. The ponds rarely, if ever, have outflow and dissipation of the herbicide would result primarily from degradation, not dilution.

Pout Pond in Uxbridge, Massachusetts, is a small 4.0 ha lake that is also used as a public swimming area. Mean

depth is about 3 meters. The Secchi disk depth at the time of application was 3.7 m, and about 5% of the surface was covered with watermilfoil (*Myriophyllum sp.*) and water-shield (*Brasenia sp.*). The second experimental pond, Springer Pond in Grafton, Massachusetts, is a 0.2 ha pond with concrete and rock sides. About 85% of the pond was covered by macrophytes, primarily fanwort (*Cabomba sp.*), waterweed (*Elodea sp.*), milfoil, and coontail (*Ceratophyllum sp.*). Average depth of Springer Pond is 1.2 meters, and secchi disk is usually about 1 meter. Flint Pond, a 40 ha pond located in Grafton, Massachusetts next to Springer Pond, was used as a control pond.

The AS formulation (18.2 kg a.i.) was applied to Pout Pond, and 0.36 kg a.i. of SRP formulation was hand-spread into Springer Pond. The AS was mixed with water in a pump reservoir and injected into the pond about 10 cm below the water surface while the boat traversed the pond. These application rates produced a theoretical concentration of 150 ppb fluridone in each pond.

Single water samples were taken from the top and the bottom of treatment ponds before fluridone application, immediately after application, and periodically for 18 months after application. At each date, a single sample was taken from mid-depth from the control pond. Samples were collected in one-liter brown polypropylene bottles, given a code number, chilled, and shipped to Morse Laboratories in Sacramento, California, via overnight express.

Samples were analyzed according to published procedures (West and Turner 1988). Water samples are passed through a Sep-Pak C18 cartridge and concentrated by rotary vacuum evaporation at 45 C with methanol and glycerol. Residues are filtered with a 0.45 micron filter and analyzed for NMF with gas chromatography.

Fluridone was extracted from water by passage through Sep-Pak C18 cartridges, eluted from the cartridges with methanol, and analyzed by high pressure liquid chromatography with UV detection at 313 nm.

RESULTS AND DISCUSSION

The rate of fluridone degradation varied between the two formulations. Application of AS to Pout Pond pro-

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duced an immediate peak of fluridone concentration that quickly dissipated to very low levels (Table 1.) Fluridone concentrations peaked at 552 ppb at the surface immediately following application, and then fell to about 120 ppb by the third day after application when mixing in the water column was more complete. Fluridone concentrations in Pout Pond decreased to about 4 ppb 531 days following treatment. Slow release pellets (SRP) produced a very different rate of release and degradation. The maximum concentration of fluridone (about 45 ppb) was reached 63 days after application, after which concentrations fell gradually until they were no longer detectable (< 1 ppb at 531 days).

As noted in previous work (West et al. 1983), fluridone degradation depends on both light intensity and temperature. Results from Pout Pond, where liquid fluridone was applied, support this finding. The degradation of fluridone in Pout Pond shows a seasonal pattern with more rapid dissipation in the summer and longer persistence in the winter (Table 1). In addition, the initial half life was about 40 days, compared to 15 to 19 days in ponds in Central Florida during the summer (West et al. 1990).

NMF was never detected in either of the experimental ponds. One sample from the control pond showed a very low concentration of NMF (4 ppb). No known reason could explain this result; consequently it was considered spurious. It was reported in the data set only because it was detected, although we believe it was due to interference. Thus, the results from these trials supports that of previous field research (Osborne et al. 1989, West et al 1990) in which NMF was not detected in natural environments. Our study supports previous work, even when very high concentrations of fluridone are used and/or when fluridone is applied in New England with cold water temperatures and reduced sunlight. These and previous results suggest either that breakdown pathways for fluridone are different in the field compared to breakdown under artificial laboratory conditions, or that NMF is rapidly degraded in natural aquatic environments.

LITERATURE CITED

Kennedy, Jr. G. L., 1986. Biological effects of acetamide, formamide, and their monomethyl and dimethyl derivatives. *Critical Reviews in Toxicology* 17:129-182.

TABLE 1. FLURIDONE CONCENTRATIONS (PPB) BEFORE AND AFTER APPLICATION OF AS TO POUT POND AND SRP TO SPRINGER POND. SINGLE SAMPLES TAKEN FROM TOP AND BOTTOM OF TREATED PONDS. ND - NOT DETECTABLE AT 1 PPB. SAMPLES WERE ALSO ANALYSED FOR NMF. NO NMF WAS DETECTED IN ANY OF THE SAMPLES AT A DETECTION LIMIT OF 2 PPB, EXCEPT FOR A SINGLE SAMPLE IN THE CONTROL POND WHOSE CONCENTRATION WAS 3.78 PPB (SEE TEXT).

Days After Treatment	Springer Pond		Pout Pond		Control
	Shallow	Deep	Shallow	Deep	Shallow
pre	ND	ND	ND	ND	ND
0	ND	ND	552*	366*	--
3	6.4	6.0	126	114	ND
7	19.2	13.9	109	ND	ND
14	26.8	22.4	79.2	86.4	ND
28	28.8	28.0	72.0	57.6	ND
42	11.0	13.9	50.0	52.0	ND
63	46.2	44.5	30.2	28.0	ND
91	32.4	31.6	33.6	37.6	ND
128	36.4	36.4	28.2	8.4	ND
180	23.0	24.8	15.2	16.4	ND
295	4.2	4.4	10.0	10.0	ND
394	4.2	4.3	6.6	6.6	ND
450	(No samples)		4.6	4.8	ND
531	ND	ND	4.4	3.5	ND

Osborne, J. A., S. D. West, R. B. Cooper, and D. C. Schmitz. 1989. Fluridone and N-methylformamide residue determination in ponds. *Journal of Aquatic Plant Management* 27:74-78.

Saunders, D. G. and J. W. Mosier. 1983. Photolysis of the aquatic herbicide fluridone in aqueous solutions. *J. Agric. Food. Chem.* 3:237-241.

West, S. D., K. A. Langeland, and F. B. Laroche. 1990. Residues of fluridone and a potential photoproduct (N-Methylformamide) in water and hydrosol treated with the Aquatic Herbicide SONAR. *J. Agric. Food. Chem.* 38:315-318.

West, S. D., R. O. Burger, G. M. Poole, and D. H. Mowrey. 1983. Bioconcentration and field dissipation of the aquatic herbicide fluridone and its degradation products in aquatic environments. *J. Agric. Food. Chem.* 31:579-585.

West, S. D. and L. G. Turner. 1988. Determination of residue levels of the aquatic herbicide fluridone and a potential photoproduct (N-methylformamide) in waters. *J. Assoc. Anal. Chem.* 71:1049-1053.

Williman, P. E. Stenographic record, 1987, EDC Project No. AV 6-16-86, State of New York, Department of Environmental Conservation, Vol. 23, 209 pp.