

Interaction of Formulation and Soil Components on the Aqueous Concentration of Fluridone¹

M. A. MOSSLER, D. G. SHILLING, K. E. MILGRAM, AND W. T. HALLER²

ABSTRACT

Fluridone was added as an aqueous suspension (AS), 5% slow-release pellet (SRP), or a 5% pellet (5P) to deionized water which contained settled sand, kaolin, bentonite, or peat. Fluridone formulated as AS was detected in water immediately after application. Fluridone release from 5P pellets was faster than SRP pellets regardless of the time at which pellet integrity was lost. A period of 72 or 400 hours was required for total release of fluridone from the two pellet formulations when agitated vigorously or mildly, respectively. Fluridone adsorption to bentonite was non-linear (S-type), while adsorption to kaolin and peat was linear (Langmuir or L-type). Quartz sand adsorbed little (<1%) fluridone. The concentration of fluridone in solution varied with time, formulation and kaolin, bentonite, and peat, but not sand. Pellet formulations of fluridone can be used beneficially when controlled release is desired in areas characterized by sandy hydrosol. Conversely, the AS formulation may be a more appropriate choice for areas characterized by high amounts of clay or organic matter.

Key words: organic matter, clay, adsorption, sand, hydrosol, desorption.

INTRODUCTION

Fluridone (1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone), the active ingredient in the aquatic herbicide Sonar[®], is used to control submersed and emergent plants (6, 9). Sonar[®] is available in three formulations: Sonar[®] AS, Sonar[®] 5P, and Sonar[®] SRP. The latter two formulations are pellets from which fluridone is released at different rates. Formulation and application method have both been shown to affect the concentration of fluridone in treated water (2, 12). Consequently, these factors could influence weed control and therefore warrant further investigation.

Fluridone is a weak base with a pK_a of 1.7 (11). At low pH, the pyridinone ring becomes protonated and positively charged, which increases the adsorption of fluridone to negatively-charged soil particles (10). Decreased phytotoxicity has been attributed to this pH dependent phenomenon (4, 7). Fluridone adsorption is also highly correlated with the proportion of montmorillonite clay or organic matter in soil (5, 11). Herbicidal sorption is directly proportional to the adsorption coefficient (K_a) of soil and values for fluridone determined using fourteen soils ranged from 2.6 for sandy soils to 100 for muck soils (3).

Formulations have long been used to modify herbicide performance. Formulations can modify how a herbicide

¹Florida Agricultural Experiment Station Journal Series No. R-02434. Received for publication August 3, 1992 and in revised form April 15 1993.

²Former Graduate Research Assistant, Associate Professor, Laboratory Assistant, and Professor, Department of Agronomy, University of Florida, Gainesville, FL 32611. Present address of senior author: KBN Engineering and Applied Sciences, 1034 NW 57th St., Gainesville, FL 32605.

interacts with various physical and/or environmental factors resulting in enhanced efficacy. For example, formulations are used to increase herbicide efficacy in water-stressed plants (1), protect the herbicide from photodecomposition (13), reduce ion-related herbicide antagonism (8), and control release rates (12). Pellet formulations of fluridone are manufactured specifically to control rate of release into water. However, fluridone pellets sink to the bottom when applied to an aquatic system, which results in most of the herbicide being in proximity to the hydrosol. This situation could result in enhanced binding to the soil with a subsequent decrease in water concentration and weed control. In contrast, fluridone applied as an aqueous suspension is dispersed throughout the water column which decreases the tendency to interact with hydrosol (relative to the pellet formulations). Consequently, when an area to be treated is characterized by high clay or organic matter content, the use of pellets could result in reduced control due to an increase in soil adsorption.

Studies were conducted to assess the benefits or liabilities associated with the use of the three fluridone formulations because fluridone is used extensively throughout Florida in areas that differ in hydrosol composition. This was accomplished by determining the release and availability of fluridone in water as influenced by soil component and/or formulation. More effective use of fluridone through proper formulation selection is one potential use of this information.

MATERIALS AND METHODS

Release rates of formulations. A pellet of each fluridone formulation (5P or SRP) was added to 250 ml of deionized water (pH 6.9) in 250-ml centrifuge tubes and agitated vigorously or mildly at 27 C on a linear shaker. One-milliliter samples were collected over either a 72- or 500-hour period (depending on amount of agitation). The samples were first passed through a filter (0.22 μm) and then the syringe and filter were rinsed with an equal volume of methanol to remove residual fluridone. The amount of fluridone released by the pellets was determined by high performance liquid chromatography (HPLC). Samples were analyzed using a 15-cm Supelco³ C8-DB column (nominal particle size 5.0 μm) with a 70:30 methanol:water mobile phase and a flow rate of 0.75 ml/minute. Retention time for fluridone was 5.6 to 6.1 minutes. Detection of fluridone was accomplished using a UV-visible detector⁴ set at 300 nm (0.01 AUFS). The concentration of fluridone in the supernatant was calculated using known standard concentrations. Each treatment was replicated three times and each replicate was sampled once at each time interval. The entire study was conducted twice.

Adsorption to soil components. Twenty-five mg of either a peat soil⁵ (29% organic matter), kaolin⁶ (a non-expanding clay), bentonite⁶ (an expanding clay), or quartz sand⁷ were

added to 40 ml of deionized water containing either 3.8, 7.5, 15, or 30 μM fluridone (pH 6.9) in 40-ml centrifuge tubes. Mixtures were agitated using a linear shaker for 24 hours and then centrifuged to pellet suspended adsorbent. The concentration of fluridone in the solution was determined by HPLC. The amount of fluridone adsorbed to the soil was then calculated ($\mu\text{moles/g}$) by determining the difference in the amount of fluridone added and the final amount in solution. Each treatment was replicated three times and each replicate was sampled once. The entire study was conducted twice.

Interaction of soil components and formulations. Ten grams of sand, peat, kaolin, or bentonite were each added to 200 ml of deionized water (pH 6.9) in 250-ml glass flasks. After settling, enough fluridone, as Sonar[®] AS, Sonar[®] 5P, or Sonar[®] SRP, was added to achieve a concentration of 10 ppm (10 mg/l). Each pellet weighed approximately 40 mg and contained 5% (w/w) fluridone. The weights of the pellets were selected so that the maximum average concentration of fluridone that could be released into the water would theoretically yield a 10 ± 1 ppm solution. Controls were included that contained fluridone but no soil components (to account for any loss due to factors other than adsorption) and soil components but no fluridone (to account for any contamination).

Each solution was agitated using a wrist-action shaker maintained at a temperature of 27 C. The shaker was set at the slowest setting to simulate the effect of mild water turbulence. Two-milliliter aliquots were removed from the center of these flasks over 400 to 600 hours. A time period of this length ensured that the pellets released all fluridone (based on the results of the release rates study).

The samples were passed through a 0.22 μm filter which was rinsed with an equal volume of HPLC-grade methanol to remove any residual fluridone. Samples were analyzed by HPLC and the mean concentration of fluridone in the water column over time determined. Each treatment was replicated three times and each replicate was sampled once at each time interval. The study was conducted twice.

RESULTS AND DISCUSSION

Release rates of formulations. The initial release rates of fluridone from the two pellet formulations differed markedly when agitated mildly (Figure 1). After 150 hours, the release of fluridone from the 5P formulation was 100% greater than the SRP formulation with water column concentrations of 8 and 4 ppm, respectively. Approximately 400 hours were required for both pellet types to release all bound fluridone.

Fluridone was released faster from both pellet formulations when agitated vigorously (Figure 1). However, a difference in fluridone release between the 5P and SRP formulations was still apparent within the first 20 hours. Beyond this time, there was little difference in fluridone concentration between the formulations.

The release rate of fluridone is probably controlled by two factors: clay type and the integrity of the pellet. The SRP pellet is made of a clay that binds to itself more tightly than the clay used to make the 5P pellet (personal com-

³Supelco, Inc., Bellefonte, PA 16823.

⁴Perkin-Elmer Corporation, Norwalk, CT 06856.

⁵Vitagreen Inc., Polk City, FL 33868.

⁶Fisher Scientific, Fair Lawn, NJ 07410.

⁷Feldspar Corporation, Edgar, FL 32149.

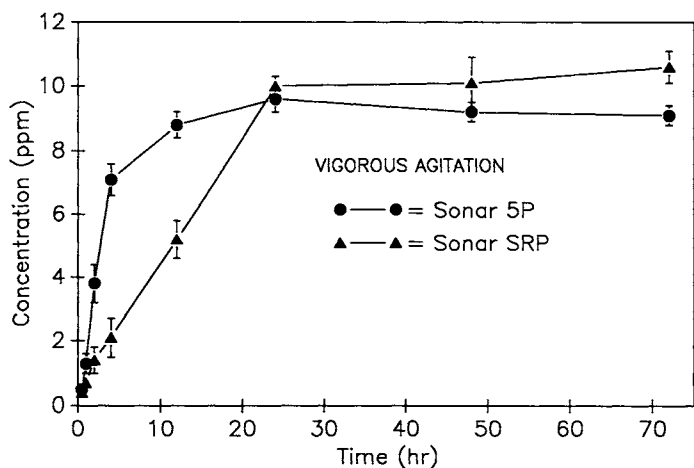
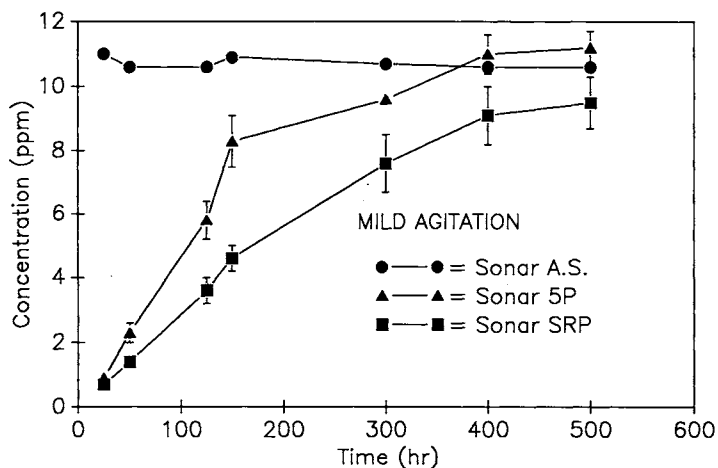


Figure 1. Effect of mild or vigorous agitation on release characteristics of Sonar® formulations (pooled mean of two studies with standard deviation).

munication, D. Farver). Vigorous agitation caused the 5P pellet to break apart quicker and release fluridone at a greater rate within 12 hours. After 24 hours, the SRP pellets lost integrity and complete release occurred. With mild agitation, integrity for both formulations was maintained for longer and contributed to extended release.

Adsorption to soil components. Bentonite adsorbed the greatest amount of fluridone when the concentration was 13 μM or greater (Figure 2). Below 13 μM , peat adsorbed the greatest amount of fluridone per unit of weight. Kaolin adsorbed fluridone in the same manner as peat, but to a lesser degree. Quartz sand adsorbed negligible amounts (<1%) of fluridone.

As illustrated by the adsorption curve, fluridone adsorption to bentonite was concentration dependent (s-type adsorption curve). This was evident when the concentration of fluridone in solution was greater than 13 μM . Once above this concentration, the adsorption of fluridone by bentonite greatly increased. Peat and kaolin exhibited L-type, or Langmuir-type adsorption, which demonstrate that there was a linear increase in adsorption as the amount of herbicide increased up to the binding capacity of each soil component. This type of adsorption is very common

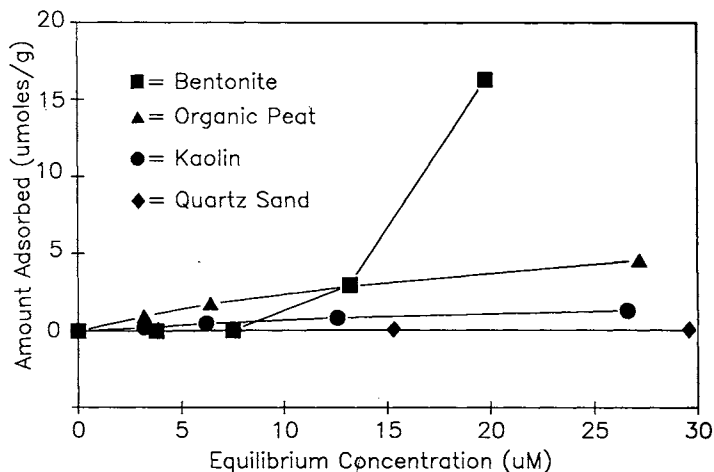


Figure 2. Fluridone adsorption curves for four different soil components (pooled mean of two studies with standard deviation).

for pesticides. Quartz sand exhibited C-type adsorption (i.e., linear adsorption), however, the slope of the curve was close to zero, indicating that concentration had very little effect on adsorption. This lack of adsorption was probably due to the inert natures of sand.

Interaction of soil components and formulations. Sand had little effect on the release rates of fluridone from either pellet formulation (Figure 3). Sand apparently increased the release rate of fluridone from both pellet formulations due to the abrading action within the flask (Figure 1 vs. Figure 3). Two to four percent of the fluridone was adsorbed by sand during the study. The low adsorptivity of sand allowed the majority of fluridone contained in the pellets to be released into the water.

In solutions containing kaolin or bentonite and the AS formulation, fluridone concentration decreased by 60% within 150 hours (Figure 3). However, the concentration of fluridone was greater throughout the study for the AS formulation versus either of the two pellet types for both clays. Very little fluridone was present in the water throughout the study for either pellet formulation.

In comparison to the AS formulation, enhanced adsorption to the clay substrates for both pellet formulations was probably due to the increased concentration of fluridone in proximity to the clay. Under natural conditions, clay would be more compressed than was the case for these studies. Adsorptivity per unit of mass of clay would decrease proportionally with amount of accessible binding sites. However, limited numbers of binding sites would not be expected under natural conditions due to the vast amount of hydrosol present in a lake bottom.

In solutions containing peat, fluridone concentration was very low throughout the study for all three formulations (Figure 3). However, higher concentrations of fluridone resulted from the AS treatment throughout the initial 350 hours. This difference again illustrates that the concentration of fluridone was greater when the herbicide was not in direct contact with the soil component (i.e., pellets laying on the bottom). After 350 hours, the concentrations of fluridone for all three formulations were similar.

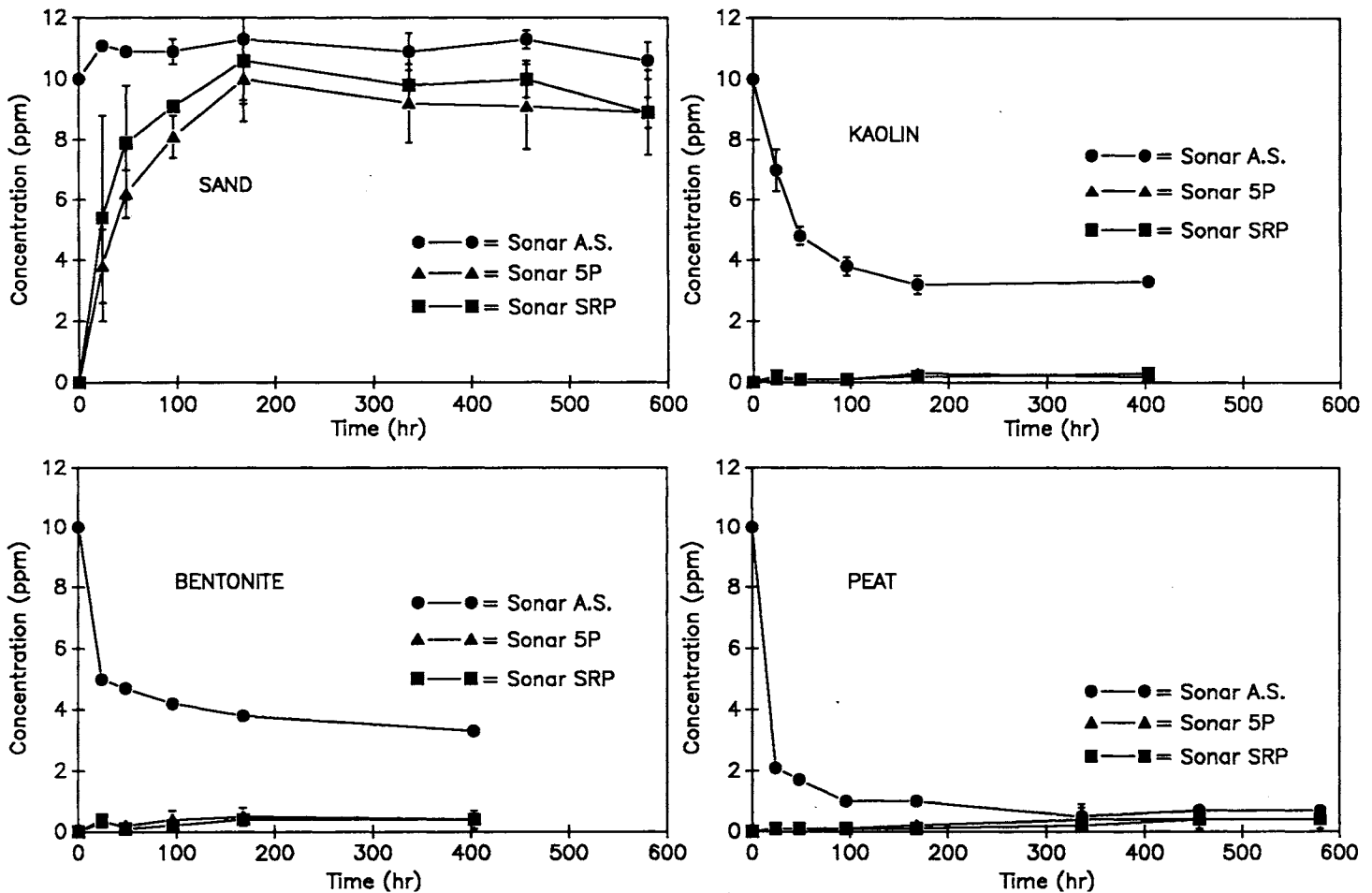


Figure 3. Influence of formulation and soil component on fluridone adsorption (mean of three replicates with standard deviation).

This situation represented actual field conditions more than the other components tested. Florida hydrosols are often high in unsettled organic matter and could adsorb substantial amounts of fluridone after application.

When fluridone is applied via pellets in waters characterized by organic or clay hydrosols, significant amounts of fluridone could be adsorbed, which would reduce the concentration in water and subsequent vegetation control. Variable results with fluridone may be caused by hydrosols of these types being present in areas treated with the pellet formulations.

ACKNOWLEDGEMENTS

These studies were supported by the Florida Department of Natural Resources and The Center for Aquatic Plants. The authors would like to thank Steve Albrecht for his assistance in preparing the graphs.

LITERATURE CITED

- Kloppenborg, D. J. and J. C. Hall. 1989. Effects of formulation and environment on adsorption and translocation of clopyralid in Canada thistle, *Cirsium arvense* (L.) Scop., and wild buckwheat, *Polygonum convolvulus* L. Weed Sci. Soc. Am. Abstr. 29:84-85.
- Langeland, K. A. and J. P. Warner. 1986. Persistence of diquat, endothal, and fluridone in ponds. J. Aquat. Plant Manage. 24:43-46.
- Loh, A. S. J. Parka, R. Albritton, and C. C. Lin. 1979. Use of adsorption coefficients and soil properties to predict fluridone herbicidal activity. Weed. Sci. 27:456-459.
- Malik, N. and D. S. H. Drennan. 1990. Effect of pH on plant uptake and soil adsorption of ¹⁴C-fluridone. Can. J. Soil Sci. 70:435-444.
- McCloskey, W. B. and D. E. Bayer. 1987. Thermodynamics of fluridone adsorption and desorption on three California soils. Soil Sci. Soc. Am. J. 51:604-612.
- McCowen, M. C., C. L. Young, S. D. West, S. J. Parka, and W. B. Arnold. 1979. Fluridone, a new herbicide for aquatic plant management. J. Aquat. Plant Manage. 17:30-33.
- Shea, P. J. and J. B. Weber. 1983. Effect of soil pH on fluridone activity and persistence as determined by chlorophyll measurements. Weed Sci. 31:347-350.
- Shilling, D. G., W. T. Haller, T. R. Willard, and M. A. Mossler. 1990. Influence of surfactants and additives on phytotoxicity of glyphosate to torpedograss. J. Aquat. Plant Manage. 28:23-27.
- Waldrep, T. W. and H. M. Taylor. 1976. 1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone, a new herbicide. J. Agric. Food Chem. 24:1250-1251.
- Weber, J. B. 1980. Ionization of buthidazole, VEL 3510, tebuthiuron, fluridone, metribuzin, and prometryn. Weed Sci. 28:467-474.
- Weber, J. B., P. H. Shea, and S. B. Weed. 1986. Fluridone retention and release in soils. Soil Sci. Soc. Am. J. 50:582-588.
- West, S. D. and S. J. Parka. 1981. Determination of the aquatic herbicide fluridone in water and hydrosol: effect of application method on dissipation. J. Agric. Food Chem. 29:223-226.
- Zorner, P., J. Hazen, R. Evans, D. Gour, and T. Fitzgerald. 1989. The influence of DASH adjuvant in limiting photodegradation of sethoxydim on leaf surfaces. Weed Sci. Soc. Am. Abstr. 29:83.