a few weeks before treatment may also be a useful predictor of the likelihood of recovery from fluridone treatment.

ACKNOWLEDGMENTS

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LITERATURE CITED


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Photolytic Degradation of Fluridone1

MARK A. MOSSLER, D. G. SHILLING AND W. T. HALLER2

ABSTRACT

The wavelengths of light involved in the photodegradation of fluridone [1-methyl-3-phenyl-5-[3-(trifluoromethyl)-phenyl]-4-(1H)-pyridinone] were characterized by exposing the herbicide to different radiation sources and filters (delineating separate parts of the light spectrum) to determine the wavelengths active in photolysis. The half-life of fluridone exposed to mercury radiation between 310-380 nm was 212 hr. Fluridone exposed to the full spectrum of natural sunlight (between 1.4-2.9 mW·cm-2) exhibited a half-life ranging from 15 to 36 hr, but radiation above 400 nm did not degrade fluridone. Fluridone exposed to radiation between 300-400 nm exhibited a half-life of 64 hr. Further studies using filters were performed to divide the range of sunlight between 297 nm and above.

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into four regions: 297-325, 325-355, 355-380 and 380 nm
and above. The half-life of fluridone in the first two
regions was 26 and 840 hr, respectively. No photolysis oc-
curred in the two highest wavelength regions. These data
indicate that radiation between 297-325 nm is primarily
responsible for the photodegradation of fluridone.

Key words: photolysis, transmittance, absorbance, ul-
traviolet radiation, environmental fate.

INTRODUCTION

Fluridone is a relatively new aquatic herbicide which is
applied in sites utilized for fishing, swimming and other
recreational activities. Studies have been conducted to
assess the environmental fate of this herbicide (9, 10, 11, 16,
18) and a literature review by Schmitz (14) concluded that
photolysis is a process involved in the degradation of
fluridone in aquatic ecosystems. Laboratory and field
studies that have investigated the photolysis of fluridone
(12, 13, 17) support this conclusion.

Photolysis studies conducted under laboratory condi-
tions by Saunders and Mosier (13) demonstrated that
fluridone photodegradation was only slightly dependent
on pH, dissolved oxygen and concentration. The half-life
of fluridone in deionized water (D1) ranged from 28 to 55
hr. West (17) subjected fluridone to DI water to a mixture
of incandescent and black light and found a half-life of 23
hr. Saunders and Mosier (13) placed fluridone in lake
water and exposed it to sunlight over a 27 day period and
found fluridone exhibited a half-life of 12 days. Similarly,
Muir and Grift (12) exposed fluridone present in pond
water to sunlight. This treatment demonstrated that
fluridone had a half-life of 6 days over the 8 day sampling
period. Although data collected under controlled condi-
tions is extensive, in situ photolysis studies under natural
conditions (i.e., in lakes) are difficult to perform and have
not been conducted. Soil adsorption, water dispersion and
microbial interaction can impact the accuracy and preci-
sion of collected data.

The quality and amount of light (UV and visible) im-
pinging on the earth's surface varies depending on the
altitude, latitude, cloud cover and ozone concentration.
Under certain conditions, wavelengths as low as 295 nm
have been detected (7). Bartholic, Halsey and Biggs (1)
conducted experiments to determine the wavelengths of
ultraviolet light that infiltrate through the atmosphere to
the earth at Gainesville, FL. (latitude 30 N and longitude
84 W). Data collected indicated that radiation below 297
nm normally does not reach the earth's surface at this loca-
tion.

Penetration of light through water has also been shown
to vary depending on a number of factors. Radiation of
720 nm (red light) and higher has been reported to be
absorbed as much as 64%·m⁻¹ in distilled water; however,
ultraviolet radiation may penetrate to a depth of 100 m
(2). Various compounds and organisms present in natural
water systems influence penetrating light both qualitatively
and quantitatively. Organic substances such as humic acids,
fulvic acids and colloids as well as microorganisms (living
and decayed) comprise what is referred to as water color
(8). As the amount of coloring increases in natural water,
light penetration is reduced. A study of two Wisconsin
lakes demonstrated that UV radiation penetration can be
reduced from 7 m to less than 1 m in a highly colored lake
(2). Color in Florida lakes may vary as much as tenfold
depending on rainfall, time of year and the amount and
types of previously mentioned factors (5). Because water
color influences the light penetrating fluridone treated
water, the amount of photolysis could be dramatically af-
fected.

Numerous factors potentially affect the photolysis of
fluridone. Because these factors differ among water sys-
tems, the amount of photolytic degradation of fluridone
may vary extensively. In order to more accurately assess
the role of photolysis in the fate of fluridone, studies were
conducted to 1) determine the wavelengths of light primar-
ily responsible for this type of degradation and 2) deter-
mine the transmission characteristics of water of selected
Florida lakes.

METHODS AND MATERIALS

Sample Preparation. Aqueous fluridone solutions were
prepared by solubilizing fluridone (99.3%) in deionized
water, mixing for 24 hr at 40 C, cooling to room tem-
perature, and filtering through a 0.2 μm filter. To determine
the concentration of fluridone, a 25 μL injection of the
solution was analyzed using a high performance liquid
chromatograph (HPLC). Fluridone was analyzed using a
DuPont® Zorbax Gold Series C8 column (nominal particle
size 3.0 μm) with a 70:30 methanol/water mobile phase
and a flow rate of 0.75 mL-min⁻¹. The retention time of
fluridone ranged from 6.8 to 8.4 min. Detection of
fluridone was accomplished using a UV-visible detector
set at 500 nm (0.005 AUFS). The concentration of
fluridone was determined utilizing peak area, as compared
to known standard concentrations. The absorbance of the
saturated solution (11.68 ppm) was recorded on a spec-
trophotometer at 300 nm using a 1.0 cm microcuvet. A
linear regression model was developed to determine
fluridone concentration from absorbance at 300 nm.

Radiation Studies. Saturated fluridone solutions placed
in capped borosilicate vials were irradiated in a thin-layer
chromatography visualizing box with a mercury light
source which emitted radiation between 310 to 380 nm
with a peak intensity at 365 nm of 300 μW·cm⁻². Fluridone
samples were spectrophotometrically analyzed after 0, 24,
48, 72 and 96 hr of irradiation.

Natural irradiation studies were conducted for the pur-
pose of emulating natural photolytic conditions, as well as
delineating (using various filters) portions of the natural

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*Eli Lilly and Co. Indianapolis, IN 46206.
*GVWP filter. Millipore Corp. Bedford, MA 01730.
*Perkin-Elmer Corp. Norwalk, CT 06856.
*DuPont Company Bailey Mill Plaza, Chandler Mill Building, Wil-
*linston, DE 19989.
*Beckman-Gilford DU conversion. Beckman Instruments Inc. Full-
*Suprasil microcuvet. Fisher Scientific. 526 route 303 Orangeburg,
*NY 10962.
*Model CM-10 visualizing cabinet and ENF-240C light source. Spec-
tronics Corp. 956 Brush Hollow Road, Westbury, NY 11590.

light spectrum. Influence of glass type, (quartz vs. borosilicate) on rate of photolysis was also investigated. Foil wrapped controls were subjected to the same conditions as the irradiated containers in all studies. Studies were not conducted on cloudy or rainy days.

The first study was conducted between May 2-10, 1988, and August 9-26, 1988. Fluridone-saturated aqueous solutions (11.68 ppm) were placed in 3 mL quartz cuvets* (1.0 cm pathlength) and 125 mL Erhlemeyer flasks** (1 cm pathlength). Quartz cuvets transmitted all radiation above 190 nm (4). Borosilicate glass transmitted 50% of the ambient light at 290 nm, but were virtually opaque below 290 nm. Evaporation in cuvets and flasks was minimized by sealing glass cuvet covers with paraffin and rubber stoppers, respectively. Fluridone concentration was determined after 0, 5, 10, 15, 20, 25, 30, 40 and 50 hr of sequential daily solar irradiation.

Another study was conducted between June 23-30, 1988 and repeated August 5-12, 1988. Saturated fluridone solutions were placed in capped borosilicate vials and exposed to unfiltered or filtered sunlight. Sunlight filtration was accomplished with a Kodak 2A gelatin Wratten filter† which omitted all radiation below 400 nm. Samples were analyzed for fluridone after 0, 10, 20, 30 and 40 hr of irradiation.

A third study using natural sunlight was conducted between June 23-30, 1988 and repeated August 5-12, 1988. Borosilicate capped vials containing fluridone saturated solution were exposed to unfiltered or filtered sunlight. Filtration was accomplished with a Kodak 18A UV glass filter†† which transmitted solar radiation between 300-400 nm. Samples were analyzed for fluridone at 0, 10, 20, 30 and 40 hr.

The fourth natural irradiation study was conducted between October 1-20 and again during the period of October 22-November 24, 1988. Solar radiation was divided into four wavelength regions: 297-325, 325-355, 355-380 and 380 nm and above. Sample vials alone or in conjunction with three Oriel glass filters‡‡ were utilized to create the four regions. Samples were analyzed from 0 to 56 hr at 8 hr increments.

Spectral irradiance during all periods of exposure were measured daily at solar noon with a spectral radiometer and measurements were transformed to total UV-B irradiance in terms of mW·cm⁻² by the following equation from Diffey (3):

\[
UV-B = \frac{320}{290} \sum E(\lambda) \Delta \lambda,
\]

where \(E(\lambda)\) is the spectral irradiance (W·m⁻²·nm⁻¹) at wavelength \(\lambda\) nm, and \(\Delta \lambda\) is the spectral sampling interval of 1 nm.

Water Color Studies. Water was obtained from six Florida lake systems between March 7, 1988 and October 12, 1988.

Samples were refrigerated until spectrophotometric analysis could be performed. Percent transmission between 300-320 nm was determined at 300, 310 and 320 nm for each water sample in a 1.0 cm pathlength microcuvet.

Data Analysis. All studies were conducted twice and treatments replicated three times. The effect of the various irradiation treatments on fluridone are presented as percent loss. Percent loss (PL) of fluridone was determined by the following equation:

\[
PL = \frac{(\text{original conc.}) - (\text{treatment conc.})}{\text{(original concentration)}} \times 100
\]

Analysis of variance (6) was used to test for main factor effects (i.e., different types of irradiation and the effect of time) and interactions. When fluridone degradation over time was evaluated, mean values were subjected to regression analysis to develop predictive models. These models were also used to determine the half-life (time required to cause a 50% loss) of fluridone as influenced by the different ranges of irradiation.

RESULTS AND DISCUSSION

The irradiation experiments conducted with a mercury light source in the thin-layer chromatography visualizing box caused a fluridone half-life of 212 hr (Table 1). The wavelengths emitted by the mercury light source ranged from 310-380 nm which includes a portion of the wavelengths included in the UV-B region. However, the intensity of this radiation (300 \(\mu\)W·cm⁻²) was 10 times less than that of natural sunlight in the same region. This difference in intensity probably explains why the half-life of fluridone exposed with natural-unfiltered radiation was 91% less compared to that observed with artificial radiation (Table 1: 20 versus 212 hr, respectively).

The results of the first natural irradiation study (quartz versus silica) are presented in Figure 1. In the first experiment, conducted between May 2-10, 1988, both glass types exhibited 93% photolysis of fluridone over the 50 hr sampling period. Half-lives of the two glass types were 15 and 16 hr for quartz and silica respectively (Table 1). The de

<table>
<thead>
<tr>
<th>Condition</th>
<th>Wavelength (nm)</th>
<th>Half-life (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial</td>
<td>310-380</td>
<td>212</td>
</tr>
<tr>
<td>Natural-quartz Exp 1.</td>
<td>297 and above</td>
<td>15</td>
</tr>
<tr>
<td>Natural-silica Exp 1.</td>
<td>297 and above</td>
<td>16</td>
</tr>
<tr>
<td>Natural-quartz Exp 2.</td>
<td>297 and above</td>
<td>32</td>
</tr>
<tr>
<td>Natural-silica Exp 2.</td>
<td>297 and above</td>
<td>36</td>
</tr>
<tr>
<td>Natural-unfiltered</td>
<td>297 and above</td>
<td>20</td>
</tr>
<tr>
<td>Natural-filtered</td>
<td>300-400</td>
<td>64</td>
</tr>
<tr>
<td>Natural-unfiltered</td>
<td>297-325</td>
<td>26</td>
</tr>
<tr>
<td>Natural-filtered</td>
<td>325-355</td>
<td>840</td>
</tr>
<tr>
<td>Natural-unfiltered</td>
<td>355-380</td>
<td>NPD</td>
</tr>
<tr>
<td>Natural-filtered</td>
<td>380 and above</td>
<td>NPD</td>
</tr>
</tbody>
</table>

*NPD signifies no photolysis detected.

gradation rate proceeded in a quadratic manner in both glass types. In the second experiment, conducted between August 9-26, 1988, quartz and silica exhibited a 74% degradation and half-lives of 32 and 36 hr respectively. Containers were more securely sealed and degradation rates of both glass types were linear. Evaporation may have concentrated the fluridone solution towards the latter period of experiment 1, which would have resulted in an anomalous decrease in degradation. Dark controls demonstrated no photodegradation in these experiments or in any of the studies. The difference between amount of degradation in the first and second experiments could have been caused by a different amount of solar radiation. Between May 2-10, the average natural irradiance between 290-320 nm (UV-B) at solar noon was 2.9 mW-cm⁻². The average irradiance between August 9-26 was 2.3 mW-cm⁻² 14. Most importantly, the results of both studies indicated that the glass type used had no significant (p<0.05) influence on rate of photodegradation. This is because both glass types are equally transparent to solar radiation. Even though borosilicate glass is opaque to short wavelength ultraviolet radiation, at the earth’s surface these wavelengths are not present. Therefore, either glass type could be used for further studies, however, borosilicate glassware is cheaper and more convenient to use.

Results from the second irradiation study are presented in Table 1. These data indicate that photolysis of fluridone did not occur on exposure to radiation above 400 nm. The half-life of fluridone in unfiltered vials was 20 hr compared to filtered vials in which no photolysis was detected.

Results from the third irradiation study are presented in Figure 2. The UV filter utilized in this experiment allowed only radiation between 300-400 nm to penetrate the samples. The half-life of fluridone in full and filtered sunlight was 21 and 64 hr, respectively (Table 1). Rate of photolysis in UV filtered samples that lagged behind the unfiltered samples could be explained by the filters absorption curve which peaks at 365 nm. The amount of transmittance at this wavelength is approximately 80% and declines logarithmically to either side of the optimally transmitted wavelength (365 nm). Therefore, 100% of the radiation between 300-400 nm did not enter through this filter. This range of radiation coincides with the mercury light source used in artificial irradiation studies, demonstrating that radiation between 300-400 nm does appear to cause photodegradation of fluridone.

Results from the fourth natural irradiation study are presented in Figure 3. The half-lives of the lowest two wavelength ranges (297-325 nm and 325-355 nm) were 26 and 840 hr, respectively. Because this study was conducted over a longer time period (30 days) than other irradiation studies, the natural decrease in UV radiation with amount of daylight may have caused the photolysis of fluridone to

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*Personal communication. R. H. Biggs.*
proceed in a quadratic manner (i.e., a concomitant decrease in rate of degradation with a decrease in solar intensity). No detectable photolysis occurred in the higher wavelength regions (355-380 and 380 nm and above). The results from the lower two ranges indicate that wavelengths between 297-325 nm are maximally responsible for the photolysis of fluridone, while the range between 325-355 nm contributes minimally. Although fluridone absorbs strongly in the short wavelength ultraviolet range of 290-330 nm, radiation below 297 nm does not reach the earth (15). Therefore, these data taken together with published information on the quality of solar radiation demonstrate that radiation between 297-325 nm is primarily responsible for the photodegradation of fluridone under field conditions.

Percent transmission between 300-320 nm through 1 cm of water obtained from six Florida lakes is presented in Table 2. As suspected, the results indicate that ultraviolet radiation is differentially absorbed by lake water. Lake Mize (a highly colored lake) showed the lowest transmittance, while other lakes were higher and similar to each other. Due to the strong absorbance of UV radiation by materials in these waters, deep penetration of this type of radiation is limited. This is in contrast to the depths of penetration observed in distilled water (2). These data indicate that the rate of photolysis in different lakes may vary greatly depending on the inherent water color of the system. This also explains the many different half-lives reported in the literature.

In conclusion, both artificial and natural irradiation studies demonstrated that radiation between 297-325 nm is maximally responsible for the photodegradation of fluridone. In addition, color of natural waters can vary the amount of ultraviolet penetration and consequently impact the degree of photolysis of fluridone.

ACKNOWLEDGEMENTS

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LITERATURE CITED


Table 2. Percent transmission of radiation between 300-320 nm through 1 cm of water in six Florida lakes.

<table>
<thead>
<tr>
<th>Lake</th>
<th>Wavelength (nm)</th>
<th>300</th>
<th>310</th>
<th>320</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mize</td>
<td></td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>13</td>
</tr>
<tr>
<td>Orange</td>
<td></td>
<td>62</td>
<td>68</td>
<td>71</td>
<td>67</td>
</tr>
<tr>
<td>Pierce</td>
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<td>74</td>
<td>78</td>
<td>74</td>
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<tr>
<td>Istokpoga</td>
<td></td>
<td>71</td>
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<td>77</td>
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