Environmental Science
Processes & Impacts

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| Journal: | *Environmental Science: Processes & Impacts* |
| Manuscript ID | EM-ART-12-2023-000537.R1 |
| Article Type: | Paper |
| | |

# Laboratory measurements underestimate persistence of the aquatic herbicide fluridone in lakes

*Sydney R. Van Frost[1], Amber M. White[2], Josie M. Jauquet[1], Angela M. Magness[3], Katherine D. McMahon[1,3*], and Christina K. Remucal[1,2*]*

[1]Department of Civil and Environmental Engineering

University of Wisconsin – Madison

Madison, WI 53706 USA

[2]Environmental Chemistry and Technology Program

University of Wisconsin – Madison

Madison, WI 53706 USA

[3]Department of Bacteriology

University of Wisconsin – Madison

Madison, WI 53706 USA

* Corresponding author addresses:

Christina Remucal: 660 N. Park St., Madison, WI 53706; email: remucal@wisc.edu; telephone: (608) 262-1820.

Katherine McMahon: 1550 Linden Drive, Madison WI 53706; email: trina.mcmahon@wisc.edu; telephone: (608) 890-2836.

**Abstract**

Fluridone is an aquatic herbicide commonly used to treat invasive freshwater plant species such as Eurasian watermilfoil, hydrilla, and curly-leaf pondweed. However, required exposures times are very long and often exceed 100 days. Thus, understanding the mechanisms that determine the fate of fluridone in lakes is critical for supporting effective herbicide treatments and minimizing impacts to non-target species. We use a combination of laboratory and field studies to quantify fluridone photodegradation, as well as sorption and microbial degradation in water and sediment microcosms. Laboratory irradiation studies demonstrate that fluridone is susceptible to direct photodegradation with negligible indirect photodegradation, with predicted half-lives in sunlight ranging from 2.3 days (1 cm pathlength) to 118 days (integrated over 1 meter). Biodegradation is attributable to microbes in sediment with an observed half-life of 57 days. Lastly, fluridone sorbs to sediments ($K_{oc} = 340 \pm 28$ L kg$^{-1}$); sorption accounts for 16% of fluridone loss in the microcosm experiments. While the laboratory results indicate that all three loss pathways can influence fluridone fate, these controlled studies oversimplify herbicide behavior due to their inability to replicate field conditions. Fluridone concentration measurements in a lake following commercial application demonstrate a half-life of >150 days, indicating that the herbicide is very persistent in water. This study illustrates why caution should be used when relying on laboratory studies to predict the fate of pesticides and other polar organic compounds in the environment.

**Environmental Significance Statement**

Fluridone is an herbicide that is intentionally applied to aquatic environments to combat the growth of invasive plant species. Fluridone requires a long exposure time in order to be effective, necessitating an understanding of its fate and behavior in the environment to optimize herbicide

efficacy and prevent unintended harm to non-target organisms. Combining both field and laboratory experiments allows for a more holistic perspective of fluridone fate under environmental conditions. This study provides insight into the photodegradation, biodegradation, and sorption of fluridone and their translation to aquatic environments. Our findings show that fluridone is susceptible to all three transformation pathways under laboratory conditions but is persistent in field environments, indicating that the laboratory experiments overpredict transformation rates.

## Introduction

Chemical control of invasive aquatic plants through herbicide application is frequently used due to its efficiency of use and selectivity towards invasive species.[1-5] To achieve an effective application, waterbodies must attain a sufficient herbicide concentration and exposure time with target plants, which is often more successfully realized through whole-lake exposures rather than localized spot treatments.[6-8] However, the unique environmental characteristics of each water body result in variable degradation rates of these herbicides. Unpredictable herbicide lifetimes may cause treatment failure, which can lead to additional applications and subsequently higher costs. Additionally, extensive herbicide application with similar modes of action can induce herbicide tolerance and resistance, which has been observed more frequently over time.[9-12] Not only does extensive herbicide use impact efficacy of herbicidal control on nuisance plant populations, but increased herbicide application can cause unintended harm to native plant communities.[13] Therefore, understanding the transformation pathways and environmental characteristics that influence herbicide degradation is crucial to developing responsible aquatic herbicide application strategies that simultaneously prevent herbicide resistance and protect native plant populations.

Fluridone (**Figure 1a**) is used globally[14-17] as an aquatic herbicide and is used to control invasive hydrilla (*Hydrilla verticillata*), curly-leaf pondweed (*Potamogeton crispus*), Eurasian watermilfoil (EWM; *Myriophyllum spicatum*), and Eurasian watermilfoil hybridized with native watermilfoil (hybrid watermilfoil; HWM; *Myriophyllum spicatum* × *Myriophyllum sibiricum*) in the United States.[1,18-24] Fluridone prevents the synthesis of biomolecules that protect the plant from photobleaching, thus inhibiting the ability of the plant to photosynthesize.[25,26] For this reason, fluridone is only effective if applied while plants are actively growing. Its unique mode of action makes it a popular alternative to auxin-mimic herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) for treating 2,4-D-tolerant HWM.[11,27] Fluridone is typically applied at a low concentration (6-26 nM) for a longer exposure time of 45-100 days[20-22] compared to 2,4-D (24 hours to >14 days)[28-30] or florpyrauxifen-benzyl (12 to 24 hours), another auxin-mimic herbicide.[31] This exposure time threshold often requires multiple fluridone applications to maintain an effective concentration.[22,32-34] However, studies have documented fluridone resistance by HWM[9] and hydrilla[35] and demonstrated evidence of sublethal effects on fish populations,[36,37] underscoring the importance of responsible herbicide applications.

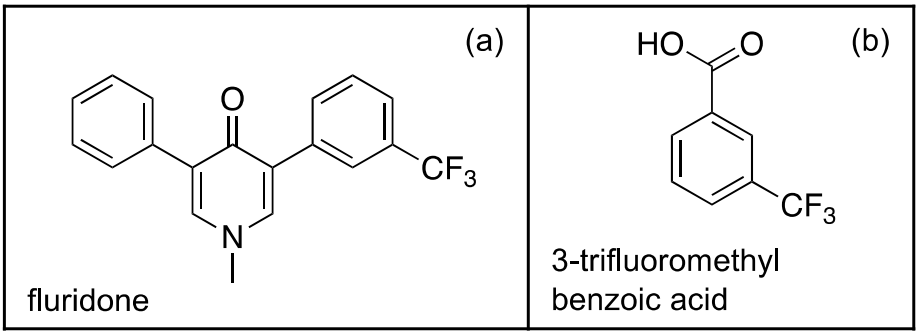


**Figure 1.** Chemical structures of (a) fluridone and (b) a major biodegradation product: 3-trifluoromethyl benzoic acid.

In aquatic environments, fluridone is stable to hydrolysis[38] and considered to be predominantly influenced by photodegradation, with reported half-lives due to photolysis of 15

hours to 12 days in ultrapure and lake water, respectively, using natural or simulated sunlight (**Electronic Supplementary Information Table S1**).[39-41] Reported photoproducts of fluridone include *N*-methylformamide, benzaldehyde, 3-trifluoromethyl-benzaldehyde, benzoic acid, and 3-trifluoromethyl benzoic acid.[33,40] While several laboratory studies investigated fluridone degradation in lake water,[40,41] the susceptibility of fluridone to dissolved organic matter (DOM) mediated indirect photodegradation has not been investigated. During indirect photodegradation, the interaction between DOM and light generates photochemically produced reactive intermediates that can increase the photodegradation rate; this process can be more important than direct photodegradation for many polar organic contaminants, including some pesticides.[42-44]

Laboratory studies also indicate that biodegradation can be an important fluridone loss pathway under some conditions, with reported half-lives of 50 days to 12 months (**Table S1**).[45,46] Although these biodegradation half-lives are longer than the reported photolysis half-lives, biodegradation may still influence the fate of fluridone in lakes. For example, the biodegradation product 3-trifluoromethyl benzoic acid (**Figure 1b**) was detected under field conditions in a small eutrophic pond and persisted up to 30 days post-application.[18]

While laboratory studies suggest that photo- and biodegradation contribute to fluridone degradation on the order of hours to weeks, limited fluridone measurements in lakes indicate that the compound can be highly persistent. Fluridone half-lives estimated from field studies range from hours to hundreds of days,[34,47] with one observation of fluridone persisting in the water column for more than a year post-treatment (**Table S1**).[22] Thus, we hypothesized that laboratory experiments underestimate the persistence of the herbicide. Sorption to sediments may also influence fluridone fate in aquatic systems. The acid dissociation constant ($pK_a$) of 12.3 indicates that the compound will be protonated at circumneutral pH values, facilitating stronger sorption to

negatively charged organic carbon in sediments.[48] Fluridone has been detected in sediments for up to a year following initial treatment, suggesting sediments are a possible reservoir for unreacted fluridone that can undergo future resuspension or uptake by plants.[34,49,50] The persistence of fluridone contributes to its transport, either through water or on suspended particles, and can lead to detection at high concentrations in untreated water bodies.[51,52] The long persistence of fluridone under field conditions in comparison to half-lives measured under laboratory conditions indicates a need for a holistic investigation into specific degradation pathways to fully evaluate the persistence of this herbicide.

The considerable exposure time requirement for fluridone treatments in lakes requires a mechanistic understanding of the environmental transformation processes that degrade fluridone. Laboratory experiments allow for the isolation of specific degradation pathways to determine their respective effects on the target compound, but they lack a direct translation to field conditions where there are competing transformation mechanisms and many environmental factors that cannot be considered in a controlled experiment. In contrast, simultaneously conducting laboratory experiments in tandem with field studies can provide a more holistic understanding of fluridone fate in aquatic environments. The goal of this study is to provide the first assessment of the combined effects of photodegradation, sediment sorption, and biodegradation on fluridone transformation under laboratory and field conditions. This study has broader implications as a model for evaluating how well laboratory studies can predict the fate of pesticides in the environment.

## Materials and Methods

**Chemicals.** All chemicals were used as received. Fluridone (99.5%) was purchased from ChemService, Inc. Dibasic potassium phosphate (ACS, 98%), monobasic potassium phosphate (ReagentPlus(R)), and 3-trifluoromethyl benzoic acid (99%) were purchased from Sigma Aldrich. Acetonitrile (HPLC grade) and formic acid (ACS, 88%) were purchased from Fisher Chemical. 2-Nitrobenzaldehyde (99%) was purchased from Acros Organics. Ultrapure water (18.2 MΩ cm) for all analyses and photochemical irradiations was obtained from a Milli-Q water purification system. pH meter calibration solutions were obtained from Aqua Solutions.

**Field sampling.** Field samples were collected from Hooker Lake in Kenosha County, Wisconsin, USA (44.56°N, 88.10°W) during a fluridone treatment in May 2022 (**Table S2**). This whole-lake treatment applied a pellet formulation of fluridone (SonarOne; 5% fluridone, 95% inactive ingredients) to target hybrid watermilfoil and curly-leaf pondweed. Pretreatment surface water was collected from near surface by grab sampling and pretreatment sediment was collected from a nearshore area by Eckman dredge or hand-coring ≤2 hours prior to treatment. Water and sediment samples were collected using the same methods every 1-2 weeks until 60 days post-treatment. Surface water samples were collected from four additional lakes via grab sampling in Wisconsin, USA for photochemical experiments (**Table S2**). All samples were stored at 4°C and in the dark until processing (**Section S2**).

**Photochemical irradiations.** Photodegradation experiments were conducted in a Rayonet merry-go-round photoreactor equipped with sixteen bulbs that emit light at 311 nm (± 22 nm width at half-max). This wavelength range is within the solar irradiance spectrum and overlaps with the absorbance spectrum of fluridone (**Figure S1**).[53] Irradiation experiments were conducted in triplicate in borosilicate glass tubes using 20 μM (6.6 ppm) fluridone in buffered (pH 7, 10 mM phosphate) ultrapure water to measure direct photodegradation. Identical solutions were held in

the dark to serve as dark controls. Indirect photodegradation was measured in lake water diluted to 3 mg-C $L^{-1}$ from four lakes to investigate the influence of dissolved organic matter composition on photolysis rates, as well as in undiluted water from Hooker Lake ([DOC] = 7.6 mg-C $L^{-1}$; **Table S2**) to quantify fluridone photolysis in the same water as the field treatment. Light intensity was quantified using 2-nitrobenzaldehyde[54] as a chemical actinometer. The fluridone concentration used in irradiations was higher than typical fluridone applications and was selected to enable detection over several orders of magnitude of loss. Calculations to convert laboratory rates to estimated rates using the full solar spectrum are discussed below.

The direct quantum yield of fluridone was calculated relative to the actinometer as described previously[53,55-57] using Equation 1:

$$\Phi_{fluridone} = \left(\frac{k_{screened,direct,\,fluridone}}{k_{direct,\,act}}\right)\left(\frac{k_{abs,\,act}}{k_{abs,fluridone}}\right)(\Phi act) \qquad \text{Eq. 1}$$

where $k_{screened,direct,fluridone}$ is the direct photodegradation rate constant for the direct control corrected for light screening ($s^{-1}$), $k_{direct,act}$ is the photodegradation rate constant of the actinometer ($s^{-1}$), $k_{abs,act}$ ($s^{-1}$) is the rate of light absorbance of the actinometer, $k_{abs,fluridone}$ ($s^{-1}$) is the rate of light absorption for fluridone, and $\Phi_{act} = 0.41$ for 2-nitrobenzaldehyde.[54] Additional details are provided in **Section S3**.

The calculated quantum yield and measured UV-vis absorption spectrum were combined with solar irradiance modeled using the Simple Model of Atmospheric Transfer of Sunshine (SMARTS)[58] to calculate the fluridone half-life in sunlight in lakes using Equation 2:

$$k_{photodegradation} = (k_{abs,sun})\,(\Phi_{fluridone}) \qquad \text{Eq. 2}$$

where $k_{abs,sun}$ is a light absorbance rate constant calculated for the horizontal global irradiance spectrum for Kenosha County, Wisconsin, USA on May 12, 2022, which was the location and date of our treatment of study. Light intensity was averaged over the time span of 6 am to 6 pm (**Figure**

**S2**) and corrected for diurnal variability (i.e., dark conditions between 6 pm and 6 am). A depth-integrated photodegradation rate was calculated as described previously.[43,56] Briefly, the photodegradation rate was calculated in 1 cm intervals through a 1-meter-deep water column (i.e., at 1 cm, 2 cm, 3 cm … 100 cm) and averaged.

**Sorption.** Pretreatment sediment from Hooker Lake (overall sediment composition: 99% muck, <1% sand, gravel, or rock)[59] was dried at 100°C for ≥8 hours. Dried sediment (1 g) was added to buffered ultrapure water (pH 7, 5 mM phosphate buffer, 100 mL) with five fluridone concentrations over the range of 1-20 μM in triplicate to create an isotherm. Samples were shaken in an incubator shaker and filtered through a 0.45 μm nylon filter after seven hours. This time frame to measure equilibrium aqueous concentrations ($C_w$) was based on preliminary sorption experiments in which equilibrium was reached after six hours (**Figure S3**). Although sediments were not sterile, biodegradation was negligible due to the short duration of these experiments (i.e., 7 hours vs. ~200 days in biodegradation experiments as described below). The concentration remaining in the sediment at equilibrium was calculated using Equation 4:

$$C_s = \frac{V\,(C_0 - C_w)}{M} \qquad \text{Eq. 4}$$

where $V$ is the volume of the solution, $C_0$ is the initial spiked concentration of fluridone, and $M$ is the mass of lake sediment used.[60]

The organic matter content of the sediment was measured through a loss-on-ignition method by combusting the dried sediment at 550°C for four hours.[61] The organic content was used to calculate the organic carbon partitioning coefficient ($K_{oc}$) of fluridone using Equation 5:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad \text{Eq. 5}$$

where $K_d$ is the sediment-specific sorption partitioning coefficient which is equivalent to the slope of the sorption isotherm and $f_{oc}$ is the fraction of organic content.[60]

**Microcosm incubations.** Biodegradation was investigated using two sets of aerobic microcosms (**Section S5**). The first set of microcosms was established using water and sediment collected from Hooker Lake immediately before the fluridone treatment. However, samples taken before 40 days were not analyzed due to improper storage. Because over half of the added fluridone was degraded by 40 days, a second set of microcosms was established with Hooker Lake water and sediment collected >3 months post-treatment to validate the fluridone biodegradation rate. Fluridone was not detected in water and sediment using high performance liquid chromatography prior to initiation. Degradation by the water column microbial community was quantified in triplicate microcosms with unfiltered lake water (3 L), while degradation by the sediment microbial community was quantified in microcosms with 0.2 μm-filtered lake water (2 L) and sediment (0.5 kg) at room temperature. Abiotic loss processes were assessed in control microcosms with 0.2 μm-filtered lake water (2 L). Microcosms were initiated with 3 μM (1 ppm) fluridone and incubated for 204 days at room temperature. Water and sediment samples were collected bi-weekly from the microcosms during the first three months and then monthly thereafter. Water samples were filtered through a 0.45 μm nylon filter and stored in a 4°C refrigerator prior to analysis. Sediment samples were collected using a serological pipette and stored in a 2.5 mL snap-cap tube in a -20°C freezer until analysis.

**Sediment extractions.** Fluridone extractions from sediment samples were conducted using 100 mg of microcosm or field sediment dried at 100°C for ≥8 hours. Dried samples were placed in Falcon tubes with 7 mL of a 50:50 methanol:water extraction solution, shaken in an incubator shaker for 2 hours, centrifuged, and syringe filtered (0.45 μm) into clean 2 mL glass amber vials

for analysis. This method had an average of (103 ± 9)% recovery over an initial fluridone concentration range of 1 to 20 μM in control experiments (**Figure S6**).

**Analytical methods.** Fluridone from laboratory experiments, 3-trifluoromethyl benzoic acid, and 2-nitrobenzaldehyde (i.e., the actinometer) were analyzed via high performance liquid chromatography (HPLC).[36] Fluridone analyzed through HPLC had a limit of detection (LOD) of 0.6 μM. Fluridone in the field samples was quantified using an Agilent Triple Quad 6460 liquid chromatograph-tandem mass spectrometer (LC-MS/MS) using positive mode electrospray ionization, which had an LOD of 2.2 nM. Ultraviolet-visible light spectra for each lake and compound were collected from 200-800 nm. Method details are provided in **Section S7**.

## Results and Discussion

**Fluridone susceptibility to direct and indirect photodegradation.** Fluridone underwent rapid photodegradation under laboratory conditions. Fluridone loss at 311 ± 22 nm (i.e., UV-B irradiation) followed first-order kinetics with a direct photodegradation rate constant in buffered ultrapure water ($k_{direct}$) of (4.1 ± 0.5) x $10^{-4}$ $s^{-1}$ ($t_{1/2}$ = 28 minutes; **Figures 2a** and **2b**). The measured direct photodegradation rate constant corresponded to a quantum yield (Φ), or reaction efficiency, of (3.8 ± 0.6) x $10^{-4}$. This value was larger than previous measurements of quantum yield of (2.7 – 5.7) x $10^{-5}$ in ultrapure water measured at pH 3 – 9 under UV-A irradiation (**Table S1**).[40] The different quantum yields may therefore be attributable to differences in experimental conditions or irradiation wavelengths.

Fluridone was irradiated in the presence of dissolved organic matter (DOM) using water from five lakes to investigate susceptibility of the herbicide to indirect photodegradation. DOM composition (i.e., aromaticity and apparent molecular weight) varied in each sample as determined

using UV-vis spectroscopy (**Table S2**). Fluridone loss in lake water also followed first-order kinetics (**Figure 2a**). The observed rate constant ($k_{obs}$) in lake water was slower than the direct photodegradation rate constant when corrected for light screening ($p$ = 0.0006, t-test; **Figure 2b**), with an average rate constant across all irradiated samples of $(3.6 \pm 0.2) \times 10^{-4}$ $s^{-1}$. The statistically slower rate constant in lake water confirmed that indirect photodegradation of fluridone was negligible under these conditions. Instead, DOM may have inhibited fluridone photodegradation, as observed previously for other target compounds.[62,63] Previous literature described similar photodegradation rates between ultrapure water and one natural water sample in sunlight.[40,64] Our study confirmed the dominance of direct photodegradation for fluridone by testing several different natural waters. Therefore, only direct photodegradation was considered for modeling half-lives under field conditions.

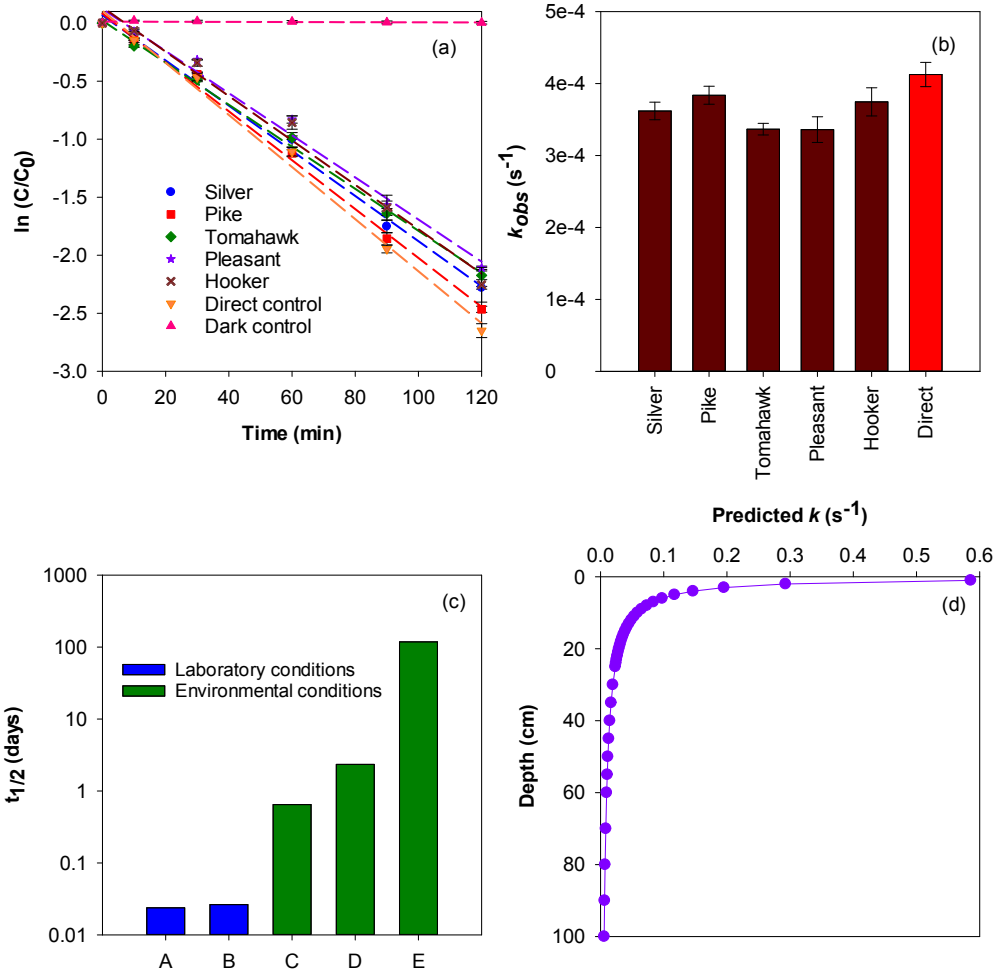


**Figure 2.** (a) First-order kinetics of fluridone loss during photochemical irradiation at 311 nm in ultrapure water (direct control) and five lake waters (**Table S2**). (b) Rate constants measured during 311 nm irradiation experiment corrected for light screening in lake waters compared to the direct control. Error bars represent standard deviation of triplicate samples. (c) Calculated fluridone photolysis half-lives where A = 311 nm irradiation (1 cm pathlength), B = laboratory conditions corrected for light screening (1 cm), C = noontime solar irradiance (1 cm), D = average irradiance with diurnal cycling (1 cm), and E = average irradiance with diurnal cycling (1 m). Note that the y-axis is on a log scale. (d) The predicted first-order photodegradation rate of fluridone under average solar irradiance conditions as a function of water depth.

The rapid photodegradation of fluridone under intense laboratory irradiation (**Figure S1**) is not indicative of the photodegradation rates expected under natural sunlight. Therefore, *in situ* photodegradation modeling was conducted using the calculated quantum yield and modeled sunlight intensities in Kenosha County, WI on May 12, 2022 (i.e., the location of Hooker Lake on

the day of treatment; **Section S3**). The half-life increased from 28 minutes under 311 nm irradiation to 16 hours under solar noon irradiation when integrated over 1 cm (i.e., near-surface conditions; conditions A and C in **Figure 2c**, respectively). Accounting for average irradiance and diurnal variability (**Figure S2**) resulted in a predicted half-life of 2.3 days over a 1 cm pathlength (condition D in **Figure 2c**) and 13 days over a 10 cm pathlength. These calculations were similar to previous reported half-lives of 7 to 12 days in mesocosm[39] and glass bottle[40] experiments (depths of 57 and 11 cm, respectively). When accounting for both diurnal variability and a depth of 1 m, the predicted fluridone half-life increased to 118 days (condition E in **Figure 2c**).

This wide range of calculated half-lives demonstrated how environmental factors could influence fluridone photodegradation rates. Using site-specific sunlight rather than intense laboratory light increased the half-life by over an order of magnitude. Importantly, the predicted half-life increased exponentially with depth (**Figure 2d**), demonstrating that depth (i.e., pathlength) was a key factor to consider under environmental conditions. Importantly, the long half-lives estimated under field conditions challenged the previous assumption that photodegradation dominates fluridone loss in aquatic systems.[39-41,46,64]

**Sorption.** Sediment-water partitioning of fluridone was measured over a concentration range of 1-20 μM after seven hours to establish a sorption isotherm (**Figure S3**). The sediment-water partitioning coefficient ($K_d$) using Hooker Lake sediment was 12 ± 1 L $kg^{-1}$. Given the organic carbon fraction of Hooker Lake sediment of (3.5 ± 0.08)%, we calculated a $K_{oc}$ value of 340 ± 28 L $kg^{-1}$. Previously reported values ranged nearly an order of magnitude from 270 to 2,460 L $kg^{-1}$.[46,65,66] Fluridone sorption has been shown to be influenced by factors such as clay content, solution pH, and temperature changes, which could explain the wide range of $K_{oc}$ values.[66,67] Our measured value agreed with the lower end of the reported range in the literature. Thus, fluridone

is moderately sorptive and partitioning to sediment may influence its fate and persistence in the environment, as well as in microcosms with sediment.

**Biodegradation of fluridone.** Degradation of fluridone was negligible throughout the duration of the 204-day microcosm study using water from Hooker Lake in the abiotic control (filtered water), as well as in the unfiltered water microcosms (**Figure 3a**). However, fluridone loss was observed in the sediment-water microcosms (**Figures 3a** and **S5**) and the loss followed pseudo-first-order kinetics with an observed half-life of 57 days. Fluridone was no longer detected in the sediment microcosms after day 143. Similar trends and kinetics were observed using the preliminary microcosms (**Figure S4**). This observed loss was comparable to reported half-lives of 50 days to 12 months measured in microcosms conducted using sediment (**Table S1**).[34,45] While this half-life indicated that the compound was relatively stable in aquatic systems, it also suggested that biodegradation could be more important than photodegradation under some conditions.

Given that sorption was expected to remove fluridone from the water column in sediment-water environments, extractions were carried out on microcosm sediment samples to quantify the amount of sorption to solids. Fluridone in the sediment was greatest at the first time point of 1 hour with a concentration of 29 μmol $kg^{-1}$, which steadily decreased over time (**Figure 3b**). The average fluridone concentration in sediment from the microcosms was (18 ± 6) μmol $kg^{-1}$ across seven samples collected over the first 60 days, which accounted for (16 ± 8)% of the initial fluridone added. This average sorption percentage was consistent with previous studies reporting 10-27% of added fluridone partitioning to the solid phase.[64,68,69] Mass balance calculations demonstrated that sorption accounted for all the fluridone lost from the aqueous phase during the first hour, but the fraction of fluridone in the sediment decreased over time (**Figure 3c**). For example, sorption only

accounted for 12% of the total added fluridone by day 49. We hypothesized that biodegradation was responsible for the remaining fluridone lost from the microcosms.

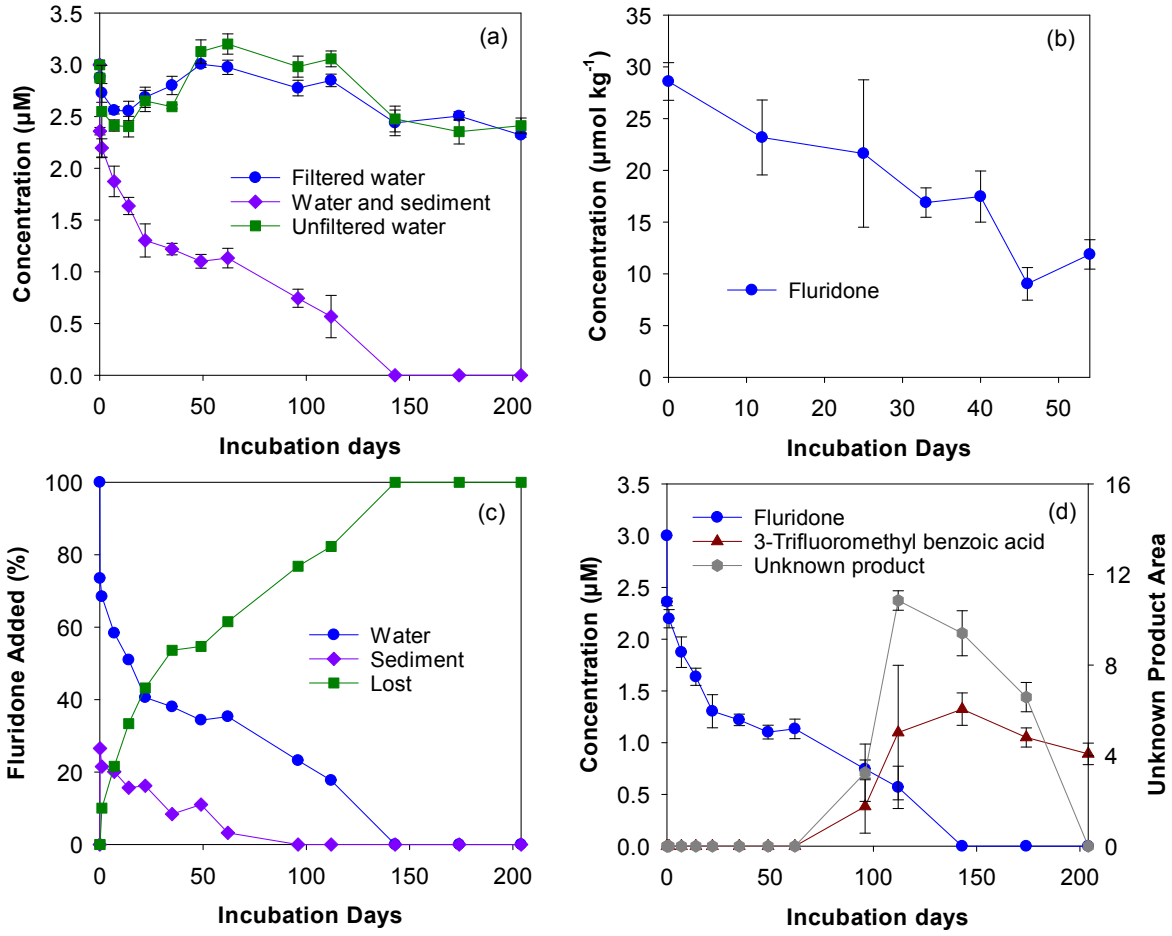


**Figure 3.** (a) Aqueous fluridone concentrations (initial concentration = 3 µM) in microcosms incubated with environmental inocula from Hooker Lake. (b) Sediment fluridone concentrations in water-sediment microcosms. Concentrations are reported as µmol of fluridone per kg of dried sediment. (c) The percent of fluridone in the water-sediment microcosms found in the water, in the sediment, and lost due to biodegradation. (d) Aqueous concentrations of fluridone and 3-trifluoromethyl benzoic acid, as well as area of an unknown product (second y-axis), detected in the water-sediment microcosms. Error bars in panels (a), (b), and (d) represent the standard deviation of triplicate reactors.

While the focus of this study was on fluridone transformation rates rather than product identification, we observed two major fluridone products by HPLC after day 60 in the sediment-water microcosms (**Figure 3d**). The transformation product 3-trifluoromethyl benzoic acid was

confirmed using an authentic standard and accumulated to a peak concentration of 1.3 μM, which corresponded to ~40% of the initial fluridone concentration. The second compound was unidentified but did not persist and was no longer detected by day 204. This compound had a shorter retention time than both fluridone and 3-trifluoromethyl benzoic acid, indicating it had a higher polarity (**Table S5**). The appearance of these products after 60 days indicated that they were not primary fluridone transformation products because loss of the herbicide was demonstrated at early timepoints through mass balance calculations (**Figure 3c**). Additional products could have been formed that were not quantified or detected in our HPLC methods; fluridone-acid (l,4-dihydro-l-methyl-4-oxo-5-[3-(trifluoromethyl)phenyl]-3-pyridinecarboxylic acid), 4-hydroxyfluridone, or the 2-hydroxy derivative have been detected in previous fluridone-sediment experiments.[46] Both compounds detected by HPLC were present in the microcosms for over 100 days, indicating they could be persistent compounds under some environmental conditions. Collectively, the mass balance (**Figure 3c**) and presence of transformation products (**Figure 3d**) provided evidence of biodegradation by the sediment microbial community.

Our observation of fluridone biodegradation only in microcosms with added sediment was consistent with the behavior of several other polar organic compounds and was likely due to higher numbers of microbes or additional nutrients in the sediments.[57,70-74] Previous studies on aquatic herbicides such as 2,4-D and florpyrauxifen-benzyl similarly observed biodegradation only in the presence of the sediment microbial community, with no loss observed due to microbes exclusively in the water column.[57,75] Ultimately, the microcosm incubations showed that biodegradation has the potential to be a key fluridone loss mechanism and that sorbed fluridone can serve as a reservoir of the herbicide.

**Fluridone behavior in lakes.** Fluridone was quantified in water and sediment following a commercial application in Hooker Lake for 60 days after treatment. This final timepoint was selected because supplemental booster fluridone treatments were planned ~2 months after the initial herbicide application, which would complicate interpretation of field data. The herbicide was applied lake-wide with a target concentration of 10 nM. Therefore, we sampled from three sites that included two opposing shorelines and one central site to characterize the 0.4-km$^2$ lake as a whole (**Figure 4a**).[59] Sediment samples were collected by the shore near sites 1 and 3. Fluridone was applied in a pellet formulation, which slowly releases fluridone into the water column.[76] Previous studies have shown that the pellet formulation of fluridone reaches peak concentration 1-3 weeks after treatment, with the rate of release being strongly dependent on the sediment type (e.g., percentages of sand, clay, and organic carbon).[3,5,49] The sediment in Hooker Lake has a moderate organic content of (3.5 ± 0.08)%, which would decrease the predicted release rate of the pellet formulation.

Aqueous fluridone concentrations at day 19 (i.e., the first timepoint after fluridone application) ranged from 7.4 nM at Site 2 to 19 nM at Site 1, corresponding to an average concentration of 12 nM. Fluridone accumulation up to ~3 weeks was consistent with previous observations of this formulation.[3,5,49] Lake water samples were collected for 40 additional days after the herbicide reached its peak concentration. The average lake-wide fluridone concentration remained steady during this time (e.g., 11 ± 4.7 nM on day 33, 11 ± 1.4 nM on day 46, and 10 ± 0.1 nM on day 60; **Figure 4b**), suggesting the lake was well mixed by day 33. Thus, fluridone remained near its target concentration of 10 nM over the 40-day period.

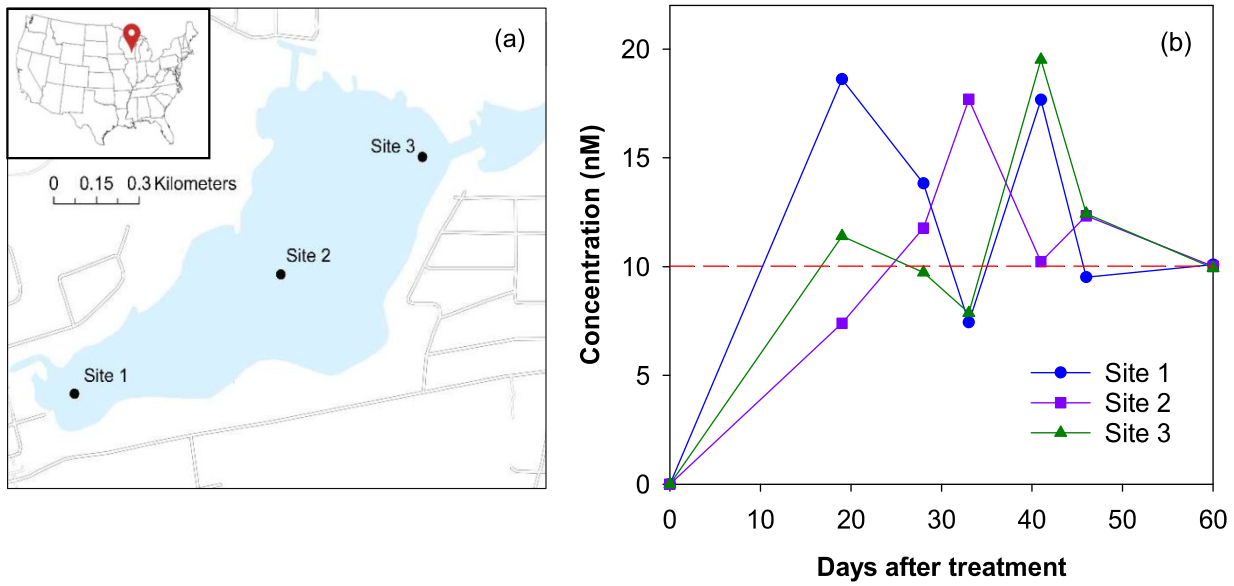


**Figure 4.** (a) All sample sites on Hooker Lake. Map made using ArcGIS. (b) Aqueous fluridone concentrations in each sample site during treatment. The dashed line is the target lake-wide fluridone concentration of 10 nM.

Fluridone was also quantified in nearshore sediment samples collected near Sites 1 and 3. Fluridone in the sediment reached a peak concentration of 4.7 nmol $kg^{-1}$ on day 19, with an average sediment concentration of 1.2 nmol $kg^{-1}$ (**Figure S7**). The average sediment fluridone concentration decreased between day 19 and day 28, which was consistent with fluridone accumulation peaking in the water around day 19. The higher initial sediment fluridone concentrations suggested initial sorption from pellet interaction with the sediments, followed by the observed accumulation of fluridone in the water due to desorption as well as release from the pellets. The average sediment concentration over days 28-60 decreased by 0.3 nmol $kg^{-1}$, indicating that the sediment did not serve as a major source of fluridone over this time period.

We predicted that both photo- and biodegradation would influence fluridone fate between days 19 and 60 (i.e., after the herbicide reached its peak concentration) based on our laboratory measurements. For example, a 20% loss of fluridone would be expected due to photolysis for 40 days using our slowest estimated half-life of 118 days (i.e., diurnal sunlight integrated over a 1 m

depth). Similarly, 40% loss of fluridone would be expected due to biodegradation for the same period using our measured half-life of 57 days. While we did not quantify fluridone in the small river leaving the lake, we also anticipated loss due to physical transport because Hooker Lake is a drainage lake. However, fluridone concentrations only experienced a total loss of 17% in the water column throughout the sampling period with an estimated half-life of >150 days (**Figure 4b**), indicating that the combined laboratory experiments underestimated the persistence of the herbicide.

There are several explanations for why the behavior of fluridone in Hooker Lake did not follow our controlled laboratory experiments. While we accounted for diurnal variability in sunlight intensity and water depth in our photodegradation calculations, other environmental factors likely slowed photolysis in the lake. First, our modeled sunlight intensity assumed clear sky conditions and did not account for cloud cover. Irradiance has a non-linear dependence on cloud cover and can decrease by nearly 70% on fully cloudy days.[77] Second, we integrated the photodegradation rate over 1 m depth because photodegradation was negligible deeper in the water column (**Figure 2d**). However, Hooker Lake was not stratified at the time of fluridone application and has a depth of up to 7 m.[59] Therefore, photodegradation was not possible in much of the water column assuming the herbicide was well mixed with depth.

Similarly, biodegradation in the field was likely slower than laboratory conditions for several reasons. First, the microcosms were incubated at room temperature (21 – 29 $^{o}$C) due to logistical reasons. However, lake water temperatures in the region around this time of year ranged from 9 – 15 $^{o}$C,[78,79] suggesting that microbial degradation would be slower because microbial activity decreases with decreasing temperature.[80-82] Second, the laboratory microcosms used higher concentrations of fluridone than the field treatment to facilitate quantification. Furthermore,

we demonstrated that biodegradation in the water column was negligible and that sediment microbes were responsible for fluridone biodegradation (**Figure 3**). Compared to field conditions, the ratio of sediment to water was also different (i.e., there was a higher sediment:water ratio in the microcosms compared to the lake). While higher biomass can increase the degradation rate and consistency of measurements, matrix-specific degradation rates can be more difficult to extrapolate to the environment.[73,83,84] Because our study only observed degradation in the sediment-water microcosms, the herbicide was applied directly to the sediment, and we used the same sediment from the field study, the sediment-water system biodegradation rate was a reasonable approximation when comparing laboratory and field data. We have successfully related laboratory-measured biodegradation rates of 2,4-D and florpyrauxifen-benzyl to field rates using a similar approach, but their biodegradation rates were faster (i.e., $t_{1/2}$ ~25 and 2.2 days, respectively).[57,75] We hypothesize the more rapid biodegradation of 2,4-D and florpyrauxifen-benzyl contributed to better laboratory to field comparisons than the fluridone microcosms,[73] but future research specifically on fluridone biodegradation is needed. While the second set of microcosms could have been primed for fluridone degradation due to the sediment being collected after initial treatment, similar fluridone loss rates were observed in microcosms conducted with pretreatment lake water and sediment (**Figures 3** and **S4**). Thus, the differences between laboratory and field sediment-water interactions, herbicide concentrations, and temperature coupled with a relatively slow fluridone biodegradation rate likely contributed to slower microbial degradation under field conditions.

**Conclusions.** This study quantified, for the first time, the photodegradation, biodegradation, and sorption of the aquatic herbicide fluridone in laboratory experiments in parallel with quantification under environmental conditions in the field. Fluridone was susceptible

to all three loss pathways under laboratory conditions and the estimated half-lives of biodegradation and photodegradation were of similar orders of magnitude. Multiple environmental factors likely influenced these processes, including water depth, seasonal variation in sunlight, temperature, microbial community composition, and sediment surface area and composition. Therefore, unique physical and chemical characteristics likely will determine whether biodegradation or photodegradation is ultimately the dominant transformation mechanism of fluridone in individual lakes.

Fluridone was persistent under *in situ* conditions and >80% of its concentration remained in the water column up to 60 days in Hooker Lake, which was longer than each of the half-lives observed in laboratory experiments. This stability further suggested that other loss processes, such as plant uptake,[85] were also minor. While the stability of the compound is beneficial for invasive species control due to the long concentration and exposure time needed for this herbicide to be effective, it raises potential concerns about fluridone persistence in lakes and possible impacts on non-target species.[36,37]

Importantly, the discrepancies between laboratory measurements and fluridone fate during the studied lake application underscore the need for caution when relying on laboratory experiments to predict the fate of organic compounds in aquatic systems. Laboratory studies are well controlled, reproducible, and enable the isolation of specific transformation or loss processes, in contrast with field studies which are logistically challenging and infeasible for compounds that are present at low concentrations and/or added to the environment at unknown rates. Therefore, laboratory-based persistence studies are widely used to predict environmental fate and to inform regulatory decisions for chemicals, including pesticides. Aquatic herbicides such as fluridone offer a unique opportunity to study transformation pathways of polar organic compounds under field

conditions. This study demonstrated that laboratory measurements can greatly overestimate degradation rates, as observed previously,[70,71,84,86,87] resulting in our assessment that compounds classified as being photolabile or biodegradable may be much more persistent in the environment than expected.

**Acknowledgements.** This work was funded by the Midwest Aquatic Plant Management Society Robert L. Johnson Memorial Grant (S.V.F. and A.M.W.), Anna Grant Birge Memorial Award (S.V.F., A.M.W., and A.M.M.) and a National Science Foundation Graduate Research Fellowship (A.M.W.). SOLitude Lake Management, especially Amy Kay, provided valuable assistance with field treatment logistics. The authors thank Michelle Nault from the Wisconsin Department of Natural Resources for technical support.

**Electronic Supplementary Information.** Additional information on field sampling methods, photochemical irradiations, sorption experiments, microcosms, and analytical methods can be found in the Electronic Supplementary Information.

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