UV Light and Temperature Induced Fluridone Degradation in Water and Sediment and Potential Transport Into Aquifer

Patrick Wickham[1], *Pramod Pandey*[1*], *Thomas Harter*[2], *Samuel Sandovol-Solis*[2]

[1]*Department of Population Health and Reproduction, University of California-Davis, Davis, California 95616*

[2]*Land Air and Water Resources Department, University of California-Davis, Davis, California 95616*

*Corresponding author:

Email: pkpandey@ucdavis.edu, Tel: + 1-530-219-6286

Capsule: This work quantifies the effect of environmental factors on the half-life of the herbicide fluridone in water and sediment and estimates possible fluridone transport through the subsurface, helping to inform sustainable herbicide application in aquatic environments.

Abstract

Fluridone is widely used in ambient water bodies to control the spread of invasive aquatic plants. While the ability of fluridone to control aquatic weeds such as water hyacinth is well reported, an improved understanding of fluridone persistence in water and sediment is still needed to determine potential residues of fluridone in the water column and bed sediment of ambient water bodies. In this study, experiments were conducted over a three-month period to examine the degradation of fluridone in saturated sediment and water under various levels of UV-light (0-1000 µW/cm^2), and temperature (4-40 °C). Results showed a large decrease in the half-life of fluridone in water with increasing UV light intensity, but in saturated sediment the impact of UV light exposure on fluridone degradation was minimal. At low temperature (4 °C), the degradation of fluridone in both water and sediment was minimal. At elevated temperature (20-40 °C), fluridone degradation was increased in water and sediment. Additionally, the persistence of fluridone in sediment was reduced by increasing sand content in the sediment matrix. Possible fluridone transport through the subsurface was estimated over a range of initial concentrations, groundwater velocities, fluridone half-lives, and fluridone sorption coefficients which may be seen in a field environment. A form of the Ogata-Banks equation which accounts for 1st order decay was used for describing the dispersion of fluridone, while a related equation from Bear 1979 was utilized to quantify advection. In all tested scenarios, maximum transport was less than 10 meters over one month of observation. Results of this study will improve our existing understanding of fluridone persistence and in water and sediment.

Keywords: *Fluridone, Degradation, Herbicide, UV, Temperature, Transport*

1. Introduction

Fluridone, 1-methyl-3-phenyl-5-[3-trifluromethyl)-phenyl]-4-(1H)-pyridinone, is a herbicide used for the control of invasive aquatic plant species such as *hydrilla*, *elodea*, and *eichnoria.* These invasive plants can outcompete native species and establish monocultures which may result in clogged waterways and decreased biodiversity (Anderson 2011; Langeland 1996; Posey et al. 1993). While fluridone is known to be an effective inhibitor of invasive aquatic plants, uncontrolled applications in ambient water bodies have the potential to increase background concentrations of fluridone in water and bed sediment which may adversely impact non-target aquatic plants (Netherland et al. 1997; Fairchild 2011; Banks and Merkle 1979). Further, elevated concentrations of fluridone in water and sediment may pose risks to aquatic life, particularly to juvenile fish, roe, mollusks, and macroinvertebrates (Parsons et al. 2009; Archambault et al. 2015; Jin et al. 2018). Conversely, low levels of fluridone application may prove ineffective to control aquatic weeds (Netherland and Getsinger 1995; Netherland and Jones 2015; Fox et al. 1996). Therefore, a thorough understanding of fluridone degradation in water and sediment is crucial to predict both background fluridone levels after application in ambient water bodies as well as potential effects on groundwater.

UV-Photolysis is known to be one of the primary mechanisms of fluridone breakdown in water, with the major catalyst being light within the UV-B range (297-325) (Mossler et al. 1989). Under UV light, fluridone is degraded into multiple photoproducts including *N*-methylformadine, benzalhydes, and benzoic acids (Saunders and Moiser 1983). Consequently, the presence of UV light at the surface of a sediment-water interphase may influence photolytic degradation in the water column and in saturated sediment. While many previous studies have examined the photolytic half-life of fluridone in water (MacDonald et al. 1996; Saunders and Moiser 1983; West et al. 1979; Muir and Grift 1982; West et al. 1983), the relationship between increasing light level and photolysis rate has not been well understood. Previous findings suggest the photolytic half-life of fluridone in water ranges from 15 hours to 90 days (Fox et al. 1996; Mossler et al. 1989). As the amount of light penetration through a given water column is typically a highly variable fraction of total incident light at surface (Mossler et al. 1989; De Haan 1993; Beeton 1958), establishing relationships between the level of UV light exposure and fluridone degradation in water could prove useful for making informed fluridone application decisions and reducing the consequential risks to aquatic life and non-target plants.

Fluridone concentrations in sediment are of interest because many fluridone-sensitive species and life stages such as mollusks and fish roe are present in or on sediment (Jacob et al. 2016; Posey et al. 1993; Hamelink et al. 1986). Fluridone concentrations in sediment can be much higher than in the overlying water column due to depositional accumulation and the absence of photolysis in bed sediment (Saunders and Mosier, 1983; West et al. 1979; Muir et al. 1980). Fluridone is highly lipophilic and bonds strongly to soil and sediment via sorption to particulate organic matter and other bonding sites in the soil matrix (Vassios 2010; Weber et al. 2004; McCloskey and Bayer, 1987). While studying fluridone degradation in soil and sediment, previous studies have linked the persistence of fluridone with organic matter, clay, and light (Anderson 1981; Langeland 1986; Shea 1983; Schroeder 1986) and it has been suggested that fluoridone's half-life may range from days to just under a year (Siemering et al. 2008; Bureau of Land Management 2005).

Currently, regulatory decisions are made by monitoring fluridone solely in the water column and there are no specific regulatory requirements for pesticide concentrations in riverine sediment. Accordingly, there is minimal information available regarding fluridone concentrations and transport in sediment. Despite this, fluridone may persist and accumulate in sediment for prolonged periods, creating elevated concentrations which may prove harmful to aquatic life (Yi et al. 2010; Siemering 2004; Jin et al. 2018). Furthermore, residual fluridone in sediment may be transported into the surrounding aquifer, affecting irrigation and drinking water. Previous field work has shown that pesticides applied directly to soils typically transmit about 5% of their annual load below the root zone (Flury 1996), but very little work has been conducted to determine the transport of pesticides which are present in fully saturated bed sediment (Gilliom 2007; Nowell et al. 1999). The Ogata-Banks equation is a commonly used analytical model which estimates transport of a solute through porous media given a steady state initial concentration (Ogata and Banks, 1961). Subsequently, Bear incorporated use of a 1st order decay constant to characterize the dispersal of contaminants which have a finite persistence (Bear 1979). This method has been well validated in laboratory environments but warrants substantial uncertainty when applied to field settings due to the extensive assumptions involved in calculations (Domenico and Schwartz 1998). Regardless this analytical model can provide valuable insight into the possible maximum transport of fluridone.

The goal of this study was to enhance the understanding of fluridone degradation in water and sediment, as well as characterize its possible transport into surrounding aquifers. Specific objectives were: 1) determine the impacts of UV-light intensity on fluridone degradation in water and sediment; 2) evaluate the effect of temperature on fluridone degradation in water and sediment; 3) assess the effect of sediment clay content on fluridone degradation; and 4) estimate the maximum possible lateral transport of fluridone through the subsurface over a one-month period.

2. Materials and Methods

2.1 Instrumentation

All fluridone concentrations in water and sediment extracts were determined using a Thermo Fisher Dionex UltiMate 3000 Pump, Autosampler, and Diode Array Detector equipped with a Restek Allure C18 5µm 150 × 4.6mm column. Centrifuging was conducted using a Fischer Scientific accuSpin 24C clinical centrifuge, and UV light was measured using a SPER Scientific UVA/B Light Meter 850009.

2.2 Material

HPLC water was procured from Fisher Chemical (Fisher Scientific, Waltham, MA). Acetonitrile and solid fluridone (99.8% purity) were purchased from Sigma-Aldrich (St. Louis, MO). Syringes and 0.22 µm Millex® filters were purchased from Becton Dickinson (Franklin Lakes, NJ) and Milipore Sigma (Jaffrey, NH) respectively. QuEChERS EN Method extract pouches and dispersive SPE were obtained from Agilent Technologies (Santa Clara, CA).

2.3 Sample Preparation

2.3.1 General Sample Preparation

Two sample types were created for these experiments, samples containing a water-sediment column (sediment samples), and samples containing only deltaic water (water samples). Water was collected from multiple areas around the California Delta and mixed to create a 'Delta Composite Sample' to be used for all experiments.

Sediment samples were prepared using sediment from French Island, Sonoma County. This sediment was dried at 30°C overnight and homogenized by mixing for 15 minutes. Then four grams of this dried sediment was placed in individual 50 mL falcon tubes along with 6 mL of delta water spiked with 10 ppm fluridone. This resulted in a saturated sediment system where sediment was topped by approximately 2 cm of water. Soil hand texture analysis supported identification of this sediment as being 'medium clay', and as such unaltered sediment samples are referred to as '100% clay' for convenience. Collected sediment had on average 0.31% nitrogen and 3.1% carbon. For carbon and nitrogen analysis, samples were first dried for 24 hours, and then crushed and homogenized using mortar and pestle. Each sample was then analyzed in triplicate using a Flash 2000 Series Elemental Analyzer, with sample weights from 10-20 mg.

Water samples were prepared by placing 40 mL of delta water containing 10 ppm fluridone in individual falcon tubes. Sediment samples were taken by simply choosing at random and removing 1 entire falcon tube per sampling event, and water samples were taken by removing two 100 µL aliquot from each falcon tube.

Periodic rehydration was required in both water and sediment samples, with frequency largely dependent on the environmental conditions present in the chamber. Rather than deltaic water, pure HPLC grade water was used for rehydration to avoid adding additional organic matter and other nutrients to the system, which may have changed the microbial activity and light transmission in the sample. Sediment samples were rehydrated to the water level present upon the experiment start. Water samples were rehydrated to maintain the same volume present on experiment start, minus the volume removed for HPLC analysis.

2.3.2 Photolysis chambers

To study the effect of UV light on photodegradation of fluridone, four photolysis chambers were designed in the lab to hold water and sediment samples over the course of the experiment. Each of the four chambers consisted of a wooden box held at room temperature (20 °C), three of which were fitted with a basic overhead UV (UV-A and UV-B) generating light maintaining a 12 hour on-off cycle. Resistors were incorporated into the design to sustain different light levels. The first chamber maintained 25 $\mu W/cm^2$ of total UV light exposure, the second chamber maintained 590 $\mu W/cm^2$, and the third maintained 1000 $\mu W/cm^2$. The fourth chamber was not fitted with a UV light, and registered 0 $\mu W/cm^2$ of total UV exposure.

Lab and field testing under UV bulbs and natural sunlight suggested some amount of UV light is filtered by the plastics composing the falcon tube. Therefore, samples were kept uncovered to allow light access to the bottom of the falcon tube. Within all photolysis chambers, UV readings were consistent across the chamber and samples were placed evenly across the chamber to allow UV penetration. As an additional precaution, samples were rearranged daily to limit preferential UV exposure in the center of the chamber. UV exposure from the top of the sediment column is also reflective of the natural environment, where most if not all UV exposure would occur at the top of the sediment column.

In addition to unaltered water and sediment samples, altered sediment mixes were prepared for these chambers to determine the effect of sediment clay content on the photolytic degradation of fluridone in sediment exposed to the three UV light levels discussed above. To create these, sediment was mixed with pure sand, creating samples containing 25%, 50%, and 75% fine or coarse sand for each photolysis chamber.

2.3.3 Incubation chambers

To test the effect of temperature on fluridone degradation, four simple incubation chambers were prepared which maintained temperatures of 4°C, 20°C, 30°C, and 40°C. Sediment and water samples were prepared for each of the 4 incubation chambers. To isolate the effect of temperature, all incubation chambers were kept in dark conditions and were covered further with a sheet of aluminum foil to reflect any incidental UV light. Due to the high temperatures involved and the lack of UV exposure, samples held in incubation chambers were fitted with cotton balls at the top of the falcon tube to minimize evaporation. Samples were checked daily for evaporation and rehydrated with pure HPLC grade water when necessary.

2.4 Fluridone extraction from sediment

While fluridone in water was analyzed in HPLC via direct injection, fluridone in sediment required use of the QuEChERS extraction method, which is well validated regarding the extraction of pesticides from soil and sediment (Bruzzoniti et al. 2014; Masiá et al. 2015; Berlioz-Barbier, 2014). In brief, the QuEChERS method consisted of an acetonitrile extraction and a dispersive Solid Phase Extraction (SPE) step. In the extraction step, 11 mL of acetonitrile was added to the sample and vortexed for 5 minutes. In the SPE step an EN Method QuEChERS Extract Pouch was added containing 1g sodium chloride, 4 g magnesium sulfate, 1 g sodium citrate, and 0.5 g sodium hydrogencitrate sesquihydrate. The sample was then shaken and vortexed for 2 minutes and centrifuged for 5 minutes at 4536 x g. A 1 mL aliquot of the supernate was then removed and placed in an EN Method QuEChERS Dispersive SPE 2 mL Fatty Samples vial containing 25 mg PSA, 25 mg C18Ec, and 150 mg magnesium sulfate. This vial was vortexed for 1 minute and centrifuged for 3 minutes at 4536 × g. Further, 1 mL of the supernate was then filtered using a syringe-drivel 0.22 µm filter and placed in 2 mL vials for UHPLC analysis. This fluridone extraction process was carried out on the entire sediment sampling including any standing water, to negate the effect of any sorption/desorption processes on the fluridone concentration,

2.5 Operating conditions of HPLC-UV detectors

All HPLC analysis was carried out on a Fisher UltiMate 3000 equipped with a Restek Allure C18 5µm 150 × 4.6 mm column. Acquisition wavelength was set at 267 nm and the carrier solvent was acetonitrile and water (60:40) with a flow rate of 1 mL/minute. Sample injection volume was 30 µL. Oven temperature was set to 26.0 °C and the total sample run time was 8 minutes. This methodology resulted in consistent Fluridone peaks at 4.20-4.23 minutes of sample retention. All samples were analyzed using Xcalibur chromatography software version No. 4.0 (Finnigan Corp.). All samples were processed via HPLC in triplicate.

2.6 Calculations and data analysis

Descriptive data analysis was conducted using Excel (Microsoft™ Office 2019). Half-life was modeled via creation of a linear trendline and associated linear decay constant. This decay constant was then converted into a half-life using the following simple equation (1).

$$t^{\left(\frac{1}{2}\right)} = \left(\frac{i}{2}\right)/\lambda \tag{1}$$

Where $t^{\left(\frac{1}{2}\right)}$= half-life, i= initial concentration (10 µg/kg), and λ= decay constant.

The error associated with this half-life prediction was similarly calculated using the following equation (2).

$$\pm t = S/\lambda \tag{2}$$

Where $\pm t$ = the standard error in the half-life prediction, S= the standard error in the modeled linear prediction of ppm (Y) using Time (X). This value was used to generate error bars for all half-life figures.

The approximated error (≈ 0.83) for all sediment samples was determined by examining both the standard deviation between all day zero sample extractions and all HPLC triplicates. Similarly, approximated error (≈ 0.5) in water samples was estimated by examining the standard deviation between all day zero water samples and their HPLC triplicates. In sediment samples, this value accounts for error inherent in the extraction method as well as standard deviation between HPLC replicates. In water samples, this value represents the standard deviation between the two water replicates as well as between HPLC replicates.

2.7 Fluridone Transport Scenarios and Calculations

A series of transport scenarios were created by considering possible variations in initial concentration, groundwater velocity, fluridone half-life, and fluridone sorption coefficient. Robust estimations of fluridone subsurface transport have not been conducted by previous studies, perhaps due to the lack of understanding regarding fluridone's half-life in sediment. Here half-life, as informed by this study and previous work, is one of the key variables in determining fluridone transport through the subsurface.

For all transport scenarios it was assumed that a consistent concentration of fluridone was maintained for a month via repeated applications in a riverbed. Further it was assumed that steady-state hydraulic gradients drive groundwater flow away from the river through a homogenous isotropic system. The value of effective porosity (θ) was set to 0.4 and matrix density (ρ) was 1.25 g/cm^3. These are typical reported values for deltaic soil with high clay and organic matter (Davis 1969; Domenico and Schwartz 1998; Weber et al. 2004). For lateral dispersivity (α_x), a value of 10 ft was assumed, which is a conservatively high value within the reported range for ponded or fully saturated systems (Vanderborght and Vereecken 2007), considering that fluridone applications typically occur in fully saturated riverbeds or ponds. Here maximum transport was defined as the distance at which fluridone concentration will be equal to 5 ppb; concentrations below this level are unlikely to cause damage to crops or non-target organisms (Hamelink et al. 1986; Jin et al. 2018).

Transport of a contaminant through porous media is governed primarily by advection and dispersion (Domenico & Schwartz 1998). Advection refers to the movement of the solute being physically carried by water through the media, typically described as a 'plug flow system'. Dispersion describes how the solute is spread to form a gradient primarily by heterogeneities in local velocity (Wang and Anderson 1995). Regarding advective transport, the position of the advective front (X_i) is determined by the lateral dispersivity (α_x), the 1st order decay constant (λ), the time elapsed since application (t), and the velocity of the contaminant (v) (Bear 1979).

$$X_i = v_t\left(\frac{(1+4\lambda\alpha_x)}{v}\right)^{\frac{1}{2}} \qquad (3)$$

To calculate the effective v for the sorbing constituent, the velocity of water (v_w) is corrected using a retardation factor (R_f).

$$v = v_w / R_f \qquad (4)$$

(R_f) is determined using properties of fluridone and the porous media: matrix density (ρ), effective porosity (θ), and the fluridone sorption coefficient obtained from batch experiments (K_d).

$$R_f = \frac{(1+\rho \times k_d)}{\theta} \qquad (5)$$

The effect of dispersion on solute concentration can be determined using a steady state form of the Ogata-Banks equation (Ogata and Banks 1961). The following adaptation of the original equation incorporates 1st order degradation to account for decay of a solute (Bear 1979):

$$C = \frac{1}{2}C_o e^\wedge\left\{\left(\frac{x}{2\alpha_x}\right) * \left[1-\left(1+\frac{4\lambda\alpha_x}{v}\right)^{\frac{1}{2}}\right]\right\} \qquad (6)$$

where C is the concentration at x, x is the lateral distance in front of the advective front, and C_o is the initial concentration. The overall transport of a solute is shown in Figure 1.

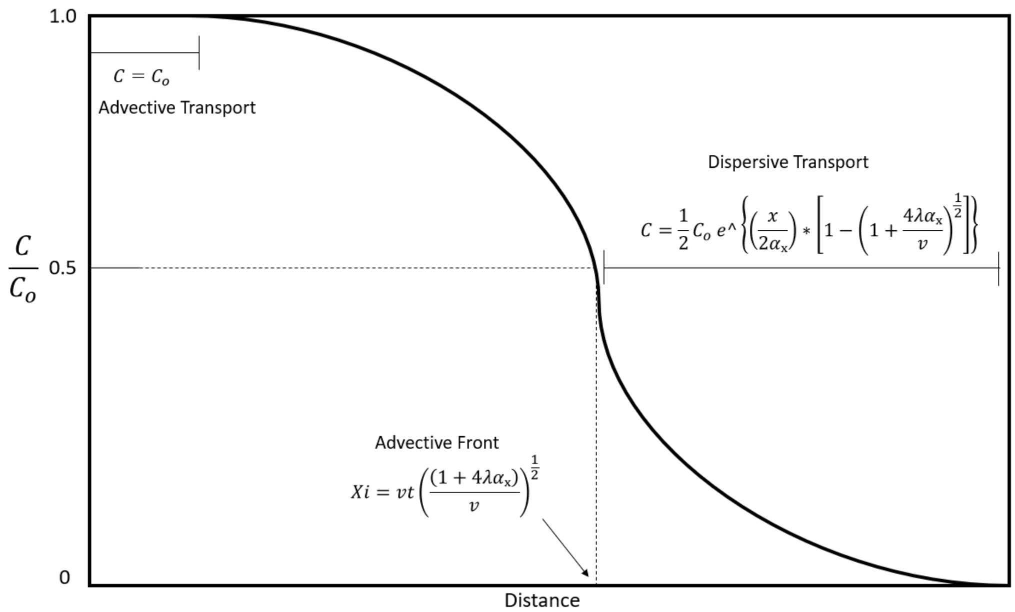

Figure 1 Governing equations and corresponding solute transport

In order to predict the maximum transport of fluridone under a variety of field scenarios, the effects of C_o, v_w, $t^{\frac{1}{2}}$, and K_d on maximum transport were examined by accounting for possible values encountered in field situations. Fluridone concentrations (C_o) in bed sediment on a per mass basis can range from 100 - 1000 ppb depending on application rate and time of application. In an accidental spill or ill managed application environment, it is possible that concentrations may rise to 10,000 ppb. When these concentrations are adjusted to reflect fluridone present in sediment pore-water using baseline K_d, (7) the range becomes approximately 10 ppb – 700 ppb.

$$C_W = C_S/K_d \tag{7}$$

Where C_W = fluridone concentration in sediment pore water and C_S = total sediment fluridone concentration.

Groundwater velocities (v_w) in riverine delta environments may vary depending on local hydraulic gradients, tidal fluctuations, surface water releases, and groundwater pumping: ranging from 0.003 to 30.48 cm/day (Wilson & Gardner, 2006; Davis, 1969; Deverel and Fujii 1988). Similarly, variation in temperature, photolysis rate, and clay content can cause fluridone's half-life in sediment ($t^{\frac{1}{2}}$) to range from 50-365 days, as informed by this work and previous studies (West et al. 1979; Banks et al. 1979; Muir and Grift 1982; Marquis et al, 1982). Fluridone's K_d, can range from around 1 to 16, depending on the sediment's organic matter and clay content (Weber et al. 2004). The baseline values selected for each of these parameters were: C_o = 700 ppb, v_w = 0.03048 cm/day, t (half-life) = 80 days, and K_d =14.

3. Results and Discussion

3.1 Impacts of UV-light intensity on fluridone degradation in water and sediment

3.1.1 Photodegradation in water

Increased UV light intensity resulted in elevated degradation of fluridone in water (Fig. 2). Under the no UV condition (0 µW/cm ^{2}), the fluridone concentration in water was decreased by 17% over the 50 days. When the UV intensity was increased to (25 µW/cm ^{2}), the fluridone level decreased by 55%. Under 590 µW/cm ^{2} and 1000 µW/cm ^{2} the fluridone concentrations were decreased by 90% and 95%, respectively. The half-life of fluridone under 0 µW/cm ^{2}, 25 µW/cm^2, 590 µW/cm^2, and 1000 µW/cm^2 was 151.5 days, 48.1 days, 30.6 days, and 27.3 days, respectively (Fig. 3).

At the lowest level of UV exposure (25 µW/cm^2), UV light appears to cause an exponential decrease in fluridone half-life, jumping from 152 days under no exposure to 48 days. After the initial jump in photolysis, increased UV exposure appears to increase photolysis linearly at a decreased slope (Fig. 3). Linear relationships between UV light exposure and photolysis rate have been observed in other pesticides such as glyphosate and malathion (Shrikant and Khambete 2014).

The fluridone half-life under UV-light seen here is within the range reported by previous studies (Table 1), between 15 hours and 60 days depending on the light source and water involved.

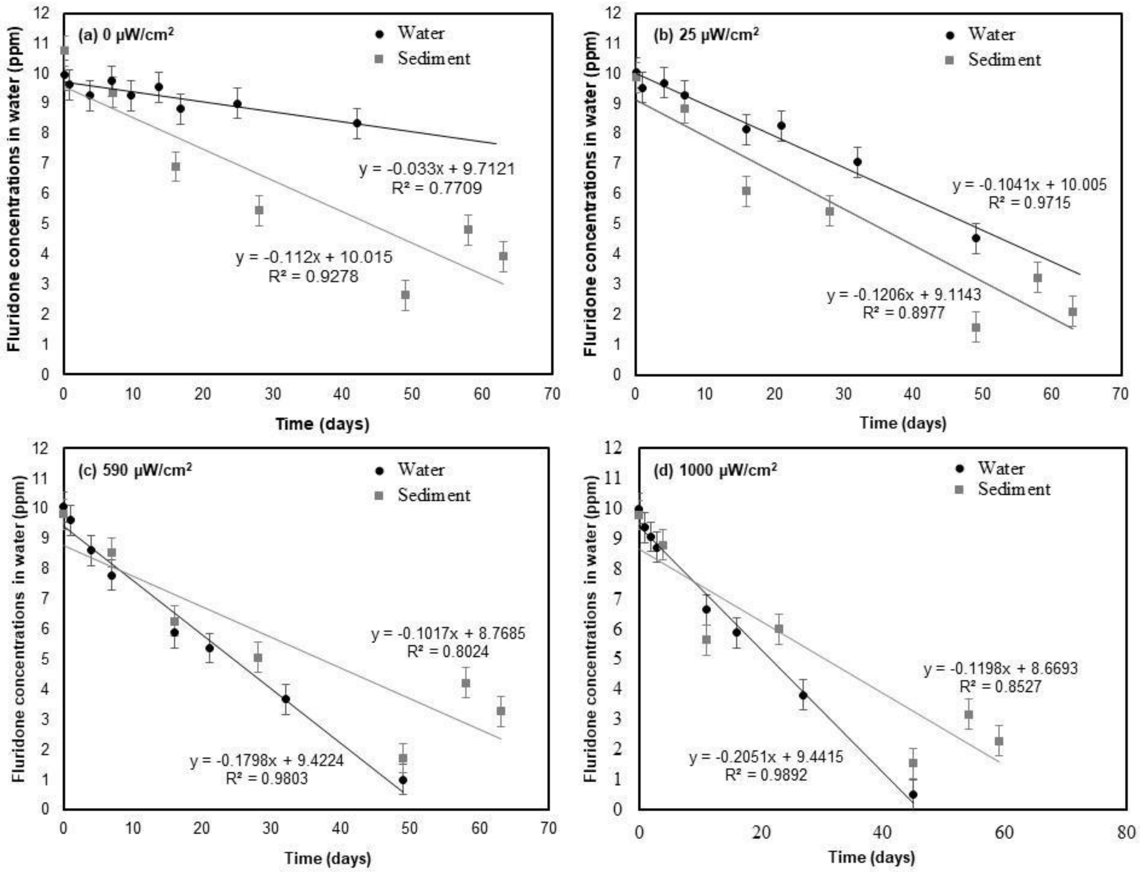

Figure 2. Degradation of fluridone in water and unaltered sediment samples exposed to UV light. Fluridone photodegradation is increased in samples exposed to increasing levels of UV light. Each point represents one tube analyzed in triplicate. Error bars in water samples represent standard deviation between HPLC replicates in day zero spiked samples. Error bars in sediment samples represent the above in addition to error in the extraction process.

The fluridone half-life under UV-light seen here is within the range reported by previous studies (Table 1), between 15 hours and 60 days depending on the light source and water involved.

Table 1. Fluridone Half-Lives Witnessed in This Study and Previous Experiments

Author(s)	Matrix	Light Source	Light Level (µw/cm^2)	Temperature (°C)	Half-Life
This Study	Delta Water	UV Lamps	0	20	151.5 Days
This Study	Delta Water	UV Lamps	25	20	48.1 Days
This Study	Delta Water	UV Lamps	590	20	27.8 Days
This Study	Delta Water	UV Lamps	1000	20	24.4 Days
This Study	Delta Water	-	-	4°C	275.1 Days
This Study	Delta Water	-	-	20°C	139 Days
This Study	Delta Water	-	-	30°C	119.9 Days
This Study	Delta Water	-	-	40°C	82.1 Days
This Study	Delta Sediment	-	-	4°C	156.3 Days
This Study	Delta Sediment	-	-	20°C	45.9 Days
This Study	Delta Sediment	-	-	30°C	53.8 Days
This Study	Delta Sediment	-	-	40°C	67 Days
West et al. 1979	DI Water	Sun Lamps and Black Lights	2000	20	23 Hours
Saunders and Moiser, 1983	DI Water	Sunlight	Unknown (~2500-4500)	-	10-15 Days
Saunders and Moiser, 1983	Lake Water	Sunlight	Unknown (~2500-4500)	-	10-15 Days
Saunders and Moiser, 1983	Lake Water	Sun Lamps and Black Lights	500	-	22 Hours
Mossler et al. 1989	DI Water	Sunlight	Unknown (~2500-4500)	-	15-21 Hours
Mossler et al. 1989	DI Water	Mercury Light 310-380 nm	300	-	8 Days
MacDonald et al. 1996	Well Water	Unfiltered Sunlight	Unknown (~2500-4500)	-	~20 Hours
MacDonald et al. 1996	Well Water	UV-B Filtered Sunlight	Unknown (~2500-4500)	-	~ 25 Days
SePro Inc Product Info	Water	Sunlight	Unknown (~2500-4500)	-	5-60 Days
Fox et al. 1996	Lake Water	Sunlight	Unknown (~2500-4500)	-	90 Days
Muir and Grift, 1982	Ponds	Sunlight	Unknown (~2500-4500)	-	2.5-3 Days
Muir and Grift, 1982	Pond Water	Sunlight	Unknown (~2500-4500)	-	6 Days
West and Parka, 1981	Pond Water	Sunlight	Unknown (~2500-4500)	-	21-26 Days
West et al. 1983	Ponds	Sunlight	Unknown (~2500-4500)	-	20 Days
Banks et al. 1979	Lufkin Fine Sandy Loam Soil	Sunlight	Unknown (~2500-4500)	-	~6.5 months
Banks et al. 1979	Miller Clay Soil	Sunlight	Unknown (~2500-4500)	-	~4 months
Muir and Grift, 1982	Pond Sediment	Sunlight	Unknown (~2500-4500)	-	~4 months
West et al. 1979	Pond Water and Hydrosoil	Sunlight	Unknown (~2500-4500)	-	1-13 days
Muir and Grift, 1982	Saturated Sediment in Flasks	-	-	~25°C	12 months
Marquis et al. 1982	Sandy Loam	-	-	~25°C	~6 months
Marquis et al. 1982	Silt Loam	-	-	~25°C	~6 months

Certain deviation between this study and previous reported values could be because this study simulated day/night conditions [12 hours day (UV light on) and 12 hours night (UV light off)], while some previous studies lab used continuous UV light exposure.

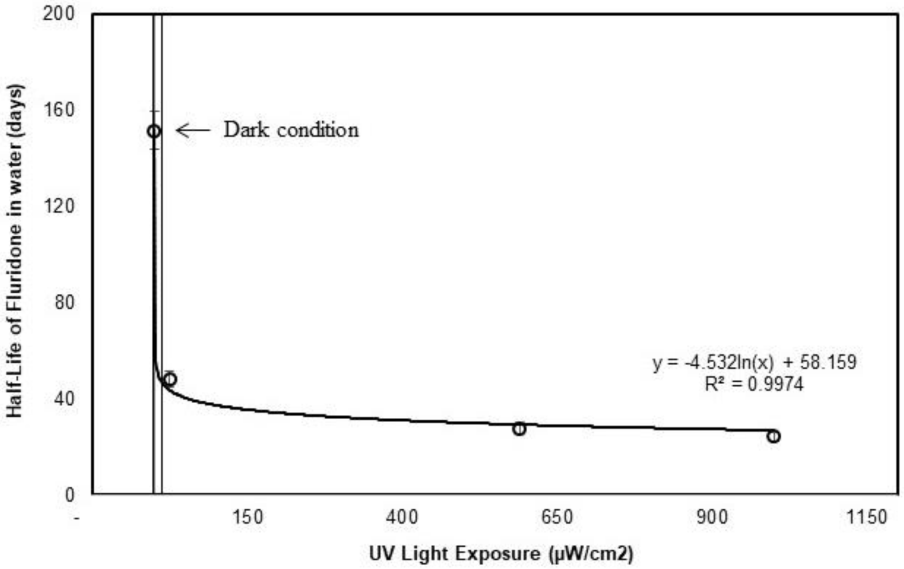

Figure 3. Half-lives of fluridone in water samples exposed to UV light. The relationship between UV light and fluridone degradation is exponential. Fluridone half-life decreases rapidly from 0-25 µW/cm2 and then gradually from 25-1000 µW/cm^2

Further, it is well established that pesticide photodegradation can change from one waterbody to another depending on the presence of high organic matter, sediment, or other contaminants (Lund-HØie and Friestad 1986; Si et al. 2004; Garbin et al. 2007; Orellana-García et al. 2015). Some deviation may also result from differences in initial spike concentration, as previous studies have demonstrated a slight correlation between initial concentration and photolytic half-life (Mossler et al. 1983; Saunders and Moiser 1983). Finally, the photolysis chambers constructed for this experiment utilized basic UV generating lamps, rather than actual sunlight or a multiple lamp setup which would more closely approximate sunlight.

Overall, these results demonstrate that even low levels of UV light can cause extensive photolysis of fluridone in aqueous solution and that there is a linear relationship between fluridone photodegradation rate and UV exposure between 25-2000 μW/cm^2.

3.1.2 Photodegradation in sediment

To understand the impacts of UV light on fluridone degradation in sediment, sediment samples were exposed with multiple levels of UV light, and subsequently fluridone concentrations were determined in sediment. One of the primary objectives here was to compare impacts of UV lights on fluridone in water and sediment. Discrptive statistics are shown in Table 2. In contrast, the rate of fluridone decay in water changed with the level of UV light. Figure 1a shows the change in fluridone concentrations over time at dark conditions. Figures 1b, 1c, and 1d show the results when sediment was exposed to 25 μW/cm ^{2}, 590 μW/cm ^{2}, and 1000 μW/cm ^{2} UV lights. While the increased level of UV light resulted in increased fluridone decay in water, the rate of fluridone degradation in sediment remained relatively unchanged (Fig. 1). Sediments and soil particles are naturally opaque, which means the penetration of light through sediment was minimal, negating effects of UV light on fluridone degradation in sediment. On the other hand, water is relatively transparent which allowed the penetration of UV light throughout the water samples and may have resulted in increased fluridone degradation in water. Further, the high reflectivity of the clay-based sediment is increased by the presence organic matter and water, both of which were present in the sediment samples prepared for this study (Gauthier et al. 2015; Tian and Philpot 2015).

As the UV wavelengths were unable to penetrate the sediment matrix to interact with particulate bound fluridone it is unlikely that sediment was subjected to considerable level of photolysis, which is known to degrade fluridone. Therefore, even in environments with very high UV light exposure, fluridone degradation in sediment did not appear to be subject to photolytic decay.

3.2 Effect of temperature on fluridone degradation

3.2.1 Water

In water, temperature considerably affected the degradation of fluridone (Fig. 4). In water stored at 4°C, a 28% reduction in fluridone was witnessed, while 20°C and 40°C experienced 32% and 60% reductions respectively. The 30°C chamber's trend suggests a reduction of about 35%, which agrees with the other results. The half-life of fluridone under 4°C, 20°C, 30°C, and 40°C was 275 days, 139 days, 120 days, and 82 days, respectively (Fig. 4; Table 1).

Like the photolysis chambers, degradation of fluridone in water held in chambers devoid of light also progressed linearly over the course of the experiment, although near the end of the experiment some of the samples begin to slightly exhibit a shoulder-shaped curve characteristic of microbial degradation (Fig. 4 D). Shoulder shaped curves have also been observed in some previous studies of fluridone persistence in water after about two months (Muir and Grift 1982; West et al. 1979).

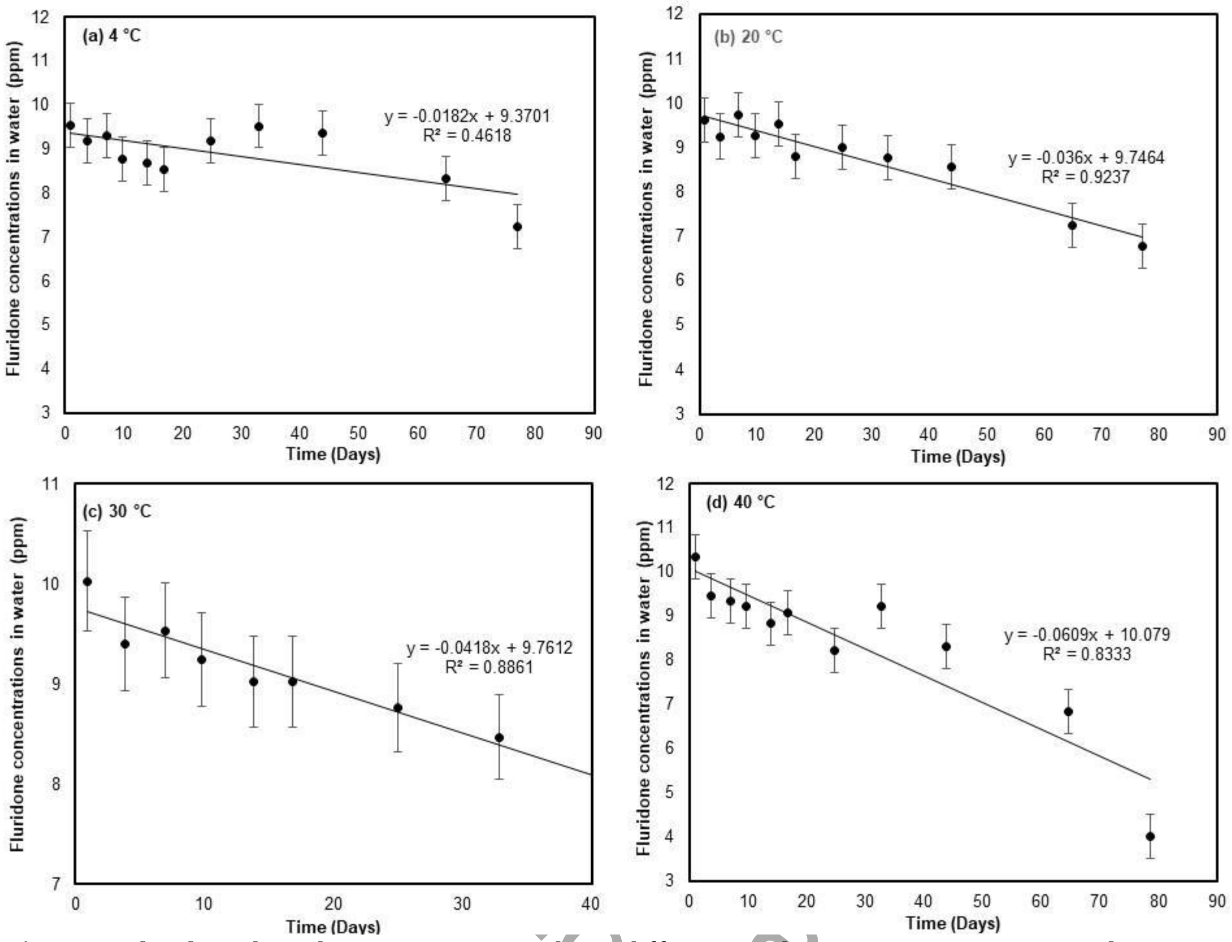

Figure 4. Fluridone degradation in water samples at different incubation temperatures. Degradation is negligible at 4°C and increases with temperature. Each point represents one tube analyzed in triplicate. Error bars represent standard deviation between HPLC replicates.

3.2.2 Sediment

Temperature appears to be a dominant variable influencing degradation in sediment (Fig. 5). At 4°C degradation was considerably slower than degradation at the higher temperatures (Table 2). Sediment samples at 4°C experienced a 30% reduction in fluridone concentration, while samples held at 20°C, 30°C, and 40°C experienced an average reduction of about 75%. Degradation at 4°C ensued with an approximate half-life of 5.13 months, while the average half-life exhibited at 20°C, 30°C, and 40°C was approximately 1.8 months (Fig. 5; Table 1).

Table 2: Descriptive statistics (mean, standard deviation, number of samples). Fluridone concentrations are shown in part per million (ppm).

Effect of Temperature (0 light 0% sand)			**Effect of UV Light (20 ºC 0% sand)**			**Effect of Clay% (20 ºC; 0 light)**	
Temperature	Water	Sediment	**UV light intensity**	Water	Sediment	**Sand Content**	Sediment
4 °C	n=11, mean=8.88 ± 0.68	n=13, mean=8.85 ± 0.99	**0 µW/cm^2**	n=24, mean=9.28 ±0.43	n=24. mean=6.75 ±2.53	**0%**	n=83, mean=6.83 ±2.57
20 °C	n=11, mean=9.28 ±0.34	n=12, mean=6.73 ±2.63	**25 µW/cm^2**	n=8, mean=8.31 ±1.82	n=49, mean=5.31 ±3.20	**25%**	n=40, mean=5.89 ±2.56
30 °C	n=6, mean=9.38 ±0.38	n=13, mean=6.44 ±2.52	**590 µW/cm^2**	n=11, mean=6.5 ±3.13	n=48, mean=5.57 ±2.94	**50%**	n=42, mean=5.11 ±3.08
40 °C	n=11, mean=8.44 ±1.72	n=12, mean=6.24 ±2.01	**1000 µW/cm^2**	n=11, mean=6.75 ±3.28	n=46, mean=5.60 ±3.29	**75%**	n=40, mean=5.07 ±3.64

When fluridone is bound in the particulate matrix of saturated sediments and not exposed to UV-light, the major cause of degradation is considered to be bacterial activity (Marquis et al. 1982)., where the fluridone compound is degraded to an acidic metabolite (1,4-dihydro-1-methyl-4-oxo-5-[3-(trifluoromethyl)phenyl]-3-pyridinecarboxylicacid). As is seen during the microbial degradation of many other pesticides and related compounds (Castillo and Torstensson 2007; Gan et al. 1999), fluridone appears to degrade fastest around 20°C-40°C, which corresponds to temperatures that facilitate the health and metabolism of mesophilic microbes (Ingraham and Bailey 1959). This mesophilic pattern is also seen in soil respiration and other forms of microbial metabolism (Lloyd and Taylor 1994; Vinola et al. 2001). These results demonstrate that the degradation of fluridone in a saturated sediment system is temperature-dependent and may be supported at equal rates above a certain threshold temperature. While degradation in sediment across all temperatures proceeded linearly over the length of the experiment, the trend may begin to resemble first order decay on a larger time scale (Fig. 5).

In sediment, degradation at all temperatures was within the large range provided by previous work (Table 1) but was relatively faster than what has been seen in some previous studies (Muir and Grift 1982; Banks et al. 1979; Marquis et al. 1982; Schroeder and Banks 1986). There are several factors unique to this experiment that may have influenced the observed degradation rates. Firstly, fluridone may have degraded faster due to the availability of water in this saturated system. A wetter environment was linked to a 30-fold increase in degradation rate in Glyphosate (Bento et al. 2016) and a similar pattern may be seen in fluridone. Secondly, this may be due in part to the ability of the microbial community to adapt to pesticide applications. After multiple applications of any pesticide, it is well documented that the microbial community will begin to increasingly support species resistant to and capable of breaking down such compounds (Vischetti et al. 2008; Felsot and Shelton 1993; Arbeli and Fuentes 2007). This phenomenon has been observed specifically with fluridone in soil after repeated applications (Banks et al. 1979). As the sediment used in this study came from an area in the California Delta that may have been exposed to incidental fluridone from nearby applications, the ability of the microbial community to degrade fluridone may have been increased via a greater abundance of microorganisms capable of metabolizing fluridone. However, the deltaic sediment collected for use in this study did not test positive for fluridone prior to inoculation, and microbial analysis of sediment was not preformed.

In addition, this study used ambient water obtained from the California Delta to inoculate these samples while most previous lab studies used chlorinated tap water, deionized water, or HPLC grade water (Marquis et al. 1982; Saunders and Mosier 1983). Using ambient water obtained from the delta may have allowed for the introduction of additional nutrients that would be present in the natural system perhaps increasing the growth of the microbial community (Doran and Zeiss 2000). This also better simulates a natural delta or riverine system where fluridone is typically applied.

Furthermore, previous lab studies held their water and sediment systems in hypoxic or anoxic environments by capping the sediment container while this study allowed unimpeded access to air via an open or cotton-topped vial. While natural water systems may become anoxic at depth, there is often a great deal of mixing in a tidally-influenced system which can allow for the introduction of oxygen (Lin et al. 2006). Previous studies suggest that fluridone in sediment degrades at slower rates when in anoxic environments (Banks et al. 1979), therefore this may have played a role in this experiment.

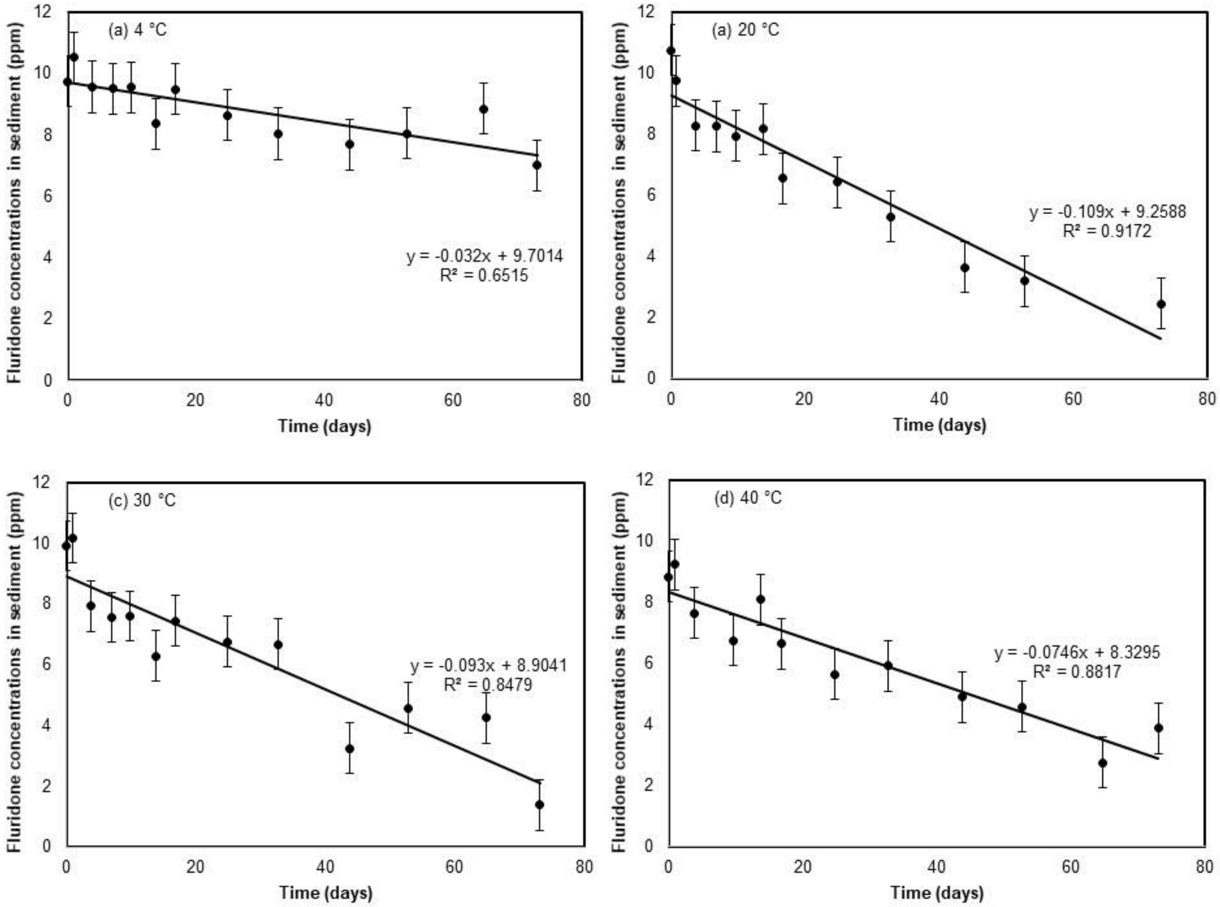

Figure 5. Fluridone degradation in sediment samples at different incubation temperatures. Degradation is limited at 4 °C compared with 20-40 °C. Each point represents one tube analyzed in triplicate. Error bars represent standard deviation between HPLC replicates and error inherent in the extraction process.

3.3 Effect of sediment clay content on Fluridone degradation

The percentage of clay within each sample appears to have an effect on the degradation rate of fluridone within sediment (Table 2), in that fluridone in pure French Island sediment degraded slower than fluridone in sediment with increasing amounts of sand (Fig. 6). Samples with 0%, 25%, 50%, and 75% sand exhibited 61%, 63%, 82%, and 86% reductions in fluridone respectively. The corresponding trend in half-life proceeds at ≈ 48 days, 53 days, 42 days, and 38 days, respectively (Fig. 6; Table 1).

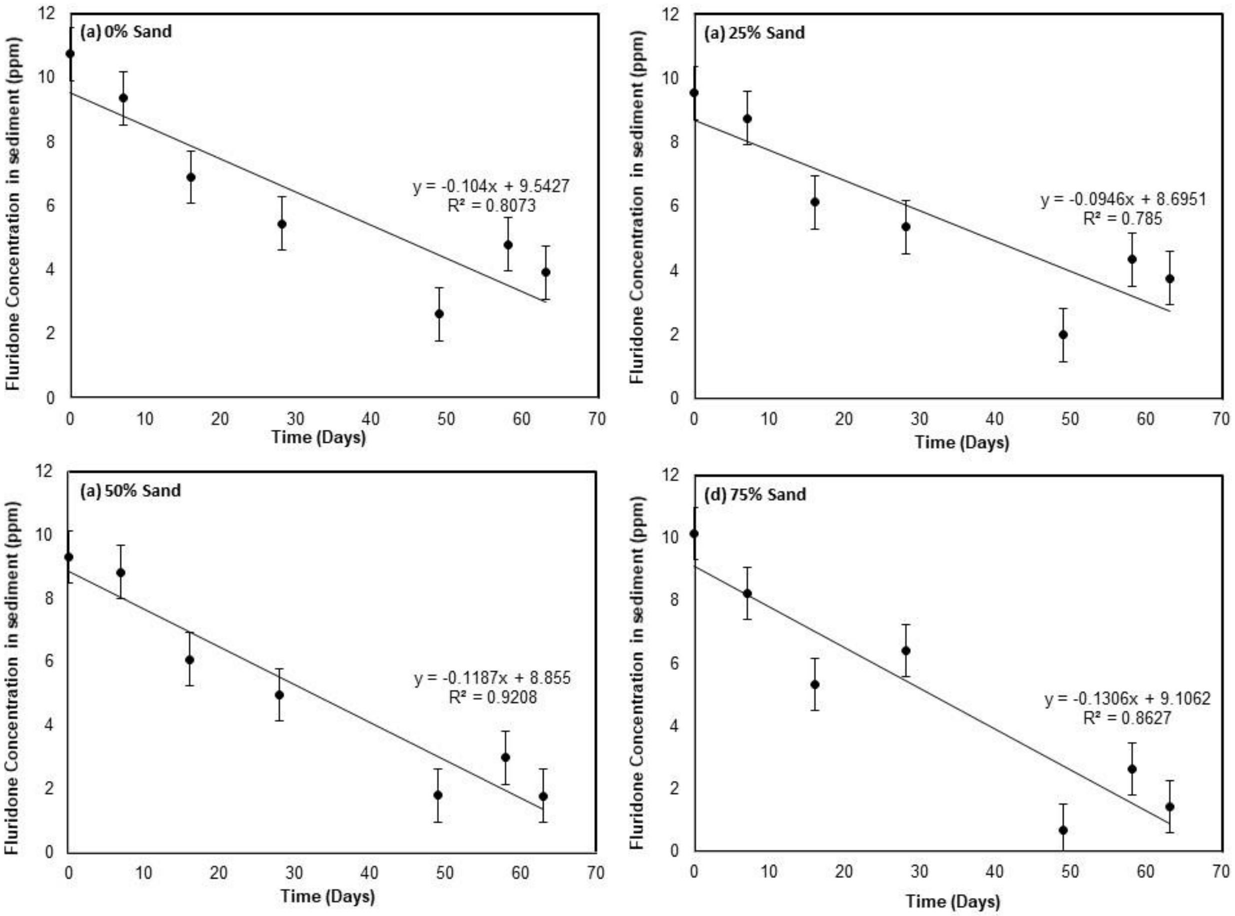

Figure 6. Fluridone degradation in sediment samples with different sand content. Fluridone degradation is increased in samples containing higher amounts of sand. Each point represents one tube analyzed in triplicate. Error bars represent standard deviation between HPLC replicates and error inherent in the extraction process.

Adding pure sand to the French Island sediment decreased the relative percentage of clay particulates and organic matter in the sediment matrix. Elevated clay content is known to decrease the bioavailability of many pesticides to plants, soil macroinvertebrates, and soil microbes (Bailey and White 1964; Yu et al. 2006). Therefore, when bound tightly to clay particulates, fluridone may be less available for microbial metabolism, as is further evidenced by previous studies which demonstrate a slower degradation of fluridone in soils with a higher clay content (Banks et al. 1979; Schroeder and Banks 1986). This pattern may also be affected by organic matter, as the presence of carbon-based organic compounds in the sediment matrix may decrease the bioavailability of fluridone to microorganisms (Bailey and White 1964; Yu et al. 2006; Castillo and Torstensson 2007).

3.4 Fluridone Transport Through Sediment and Soil

Several scenarios of varying groundwater flux, initial concentration, degradation rate, and fluridone sorption were evaluated (Table 3). Across all examined scenarios, results suggest it is extremely unlikely for fluridone to travel considerable lateral distances after application. Initial concentration was varied over 2 orders of magnitude but had very little effect on the transport of fluridone, with less than factor 3 variation between best- and worst-case scenario (≈0 to 0.23 m). Similarly, half-life was varied over an order of magnitude, from one month to one year, encompassing our experimental outcomes. Minimal sensitivity was observed from a practical standpoint with a maximum travel distance of 0.5 m in the worst-case scenario. Likewise, K_d also had minimal effect on transport, creating 0.72 meters of transport in the worst-case scenario (Table 3). The per-unit effect of K_d on transport is relatively strong, but the overall effect is limited by the small range over which fluridone K_d may occur (1-16). Groundwater velocity had a more moderate effect on fluridone transport, but still only created 9.97 m of maximum transport in the worst-case scenario of 30.48 cm/day (Table 3). For a worst-case combination of all four parameters, the maximum transport distance of concern would be about 20 m. Between the three variables examined, groundwater velocity had the greatest impact on transport due to the wide range over which it may occur, and the physics of the advection-dispersion process. These calculations suggest it is extremely unlikely for fluridone to be transported over 10 - 20 m in a typical application setting. Unless wells are completed in the immediate vicinity of the stream, it is unlikely for fluridone to pollute nearby agriculture through subsurface travel. However, horizontal wells completed underneath or near riverbeds to capture stream water could be vulnerable to potential fluridone contamination. For example, the city of Santa Rosa operates a riverbank filtration (RBF) system near the city of Wohler, which utilizes horizontal wells placed 16 meters below the Russian River (Vozza 2013; Zhang et al. 2011). Nearby, *hydrilla* have proven a recurring problem in Spring Lake and Clear Lake, outbreaks of which have historically been treated with fluridone (Dechoretz 1989; Cockreham and Netherland 2000). Were *hydrilla* to establish near the Wohler RBF site, fluridone applications could risk contaminating the Santa Rosa public water supply with herbicide. In addition to the above concerns, the low fluridone transport predicted here also underscores the possibility that fluridone may negatively impact the health of organisms which live in or interact with the bed sediment of aquatic environments due to increased accumulation in bed sediment.

Table 3. Maximum Fluridone Transport Across Variation in C_o,V_w, $t^{\frac{1}{2}}$, & in meters. Baseline values are C_o = 700 ppb, v_w = 0.03048 cm/day, $t^{\frac{1}{2}}$ = 80 days, and K_d =14.

C_o (ppb)	**10**	**100**	**200**	**500**	**700**
Maximum Transport (m)	≈0	0.14	0.17	0.22	0.23
V_w (m/day)	**0.003048**	**0.03048**	**0.3048**	**3.048**	**30.48**
Maximum Transport (m)	0.08	0.25	0.81	2.69	9.97
$t^{\frac{1}{2}}$ (days)	**30**	**50**	**80**	**120**	**365**
Maximum Transport (m)	0.18	0.21	0.25	0.30	0.50
K_d	**1**	**4**	**8**	**12**	**16**
Maximum Transport (m)	0.72	0.46	0.36	0.31	0.28

3.5 Policy Implications

In California, there are Pesticide Control Advisors (professionals with license to prescribe pesticide applications) as well as licensed Pesticide Control Applicators (individuals trained to execute the prescriptions of pesticide applications), both referred to as PCAs. PCAs applying in or near aquatic environments must obtain pesticide application permits from the National Pollutant Discharge Elimination System (NPDES) in accordance with the Clean Water Act (United States Environmental Protection Agency, 2018). When applying in areas known to contain endangered species, PCAs may also be subject to additional permitting requirements from the United States Fish and Wildlife Service, the National Marine Fisheries Service, or in the case of California, the California Department of Fish and Wildlife. In all application situations, PCAs must strictly follow the instructions present on the Environmental Protection Agency (EPA) approved pesticide label (United States Environmental Protection Agency, 2017). Because this pesticide is directly applied in ambient water bodies, PCAs must: (1) follow the concentrations specified on the label to prevent high concentrations in water that can reach and be absorbed by sediment and impact aquatic species, (2) verify that the application device (sprayer and nozzles) and the velocity of the vessel are coordinated so the pesticide concentration does not exceed the maximum allowed concentration in water bodies, (3) take a look at the weather forecast so applications are not made at low water temperatures that may increase the persistence of fluridone in the environment, and (4) use professional criteria to advise against the application of fluridone in river-reaches that exhibit exceptional habitat conditions for aquatic species (e.g. juvenile fish, roe, mollusks, and macroinvertebrates).

Results from this study may inform policy and decision makers and regulators to identify river-reaches that have high quality habitat and protect these reaches from extensive application of fluridone, because fluridone can cause adverse effects in these aquatic ecosystems. Similar to the

Groundwater Protected Areas (GWPA) concept established for certain pesticides and areas of application, there can be defined Freshwater Protected areas (FWPA) that can prevent the application of these pesticides in areas of ecological interest. In addition, regulatory agencies may decide to obtain sediment samples and monitor river-reaches where fluridone has been applied. These monitoring activities can determine whether applications have been made in ways which are protective of the natural environment. Groundwater well permitting, especially domestic or public supply wells, in the immediate vicinity (less than 20 m) of streams with fluridone applications should be avoided.

4. Conclusions

In water, results demonstrated the relationship between increasing UV exposure and decreasing photolytic half-life. Between 0-25 μw/cm^2 there appears to be a large decrease in half-life and a linear relationship is observed between 25-2000 μw/cm^2. Degradation in water was also correlated with temperature, displaying what could either be linear or shoulder-shaped degradation. Between the two, UV light has a much greater influence on the overall speed of degradation. In sediment, microbial degradation may be the dominant fluridone degradation pathway, as results showcase the strong relationship between degradation and temperature. Degradation was greatly slowed at 4°C. Additionally, persistence is reduced by increased sand content, perhaps because fluridone present in a sand matrix exhibits increased microbial bioavailability. The half-lives exhibited here in sediment were faster than the reported values of some previous studies, suggesting that water saturation, oxygenated environments, and repeat applications of fluridone may impact degradation rates. Once fluridone is present in sediment its transport is determined primarily by groundwater velocity and is limited to <10 m over a one-month period. Overall, results demonstrate how the different degradation pathways which dominate in water and sediment can create very different timelines for fluridone persistence. Within these systems UV light exposure, temperature, and clay content will further affect the persistence of fluridone.

ACKNOWLEDGMENT

The material presented here is based on work supported by California Department of Parks and Recreation (Agreement no. C1670803) and California Department of Water Resources. Any opinions, findings, citations, statements, conclusions, and recommendations are those of authors and do not necessarily reflect the views of the sponsoring agencies.

Funding

The work presented in this paper was funded by California Department of Parks and Recreation and California Department of Water Resources.

Availability of data and materials

All data supporting the results & discussion, and conclusions of this study are included in the manuscript.

Consent for publication

All authors gave their consent for publication.

Competing Interests

All authors declare that they have no financial and non-financial completing interests in this manuscript.

Ethical approval

This article does not contain any studies with either human participants or animals. Ethical approval and consent to participate is not required.

References

Anderson, L.W. 2011. “Freshwater plants and seaweeds”. In: Simberloff, D. and M. Rejmanek. Encyclopedia of Biological Invasions. Berkeley: University of California Press.

Arbeli, Z., Fuentes, C. L., 2007. Accelerated biodegradation of pesticides: An overview of the phenomenon, its basis and possible solutions; and a discussion on the tropical dimension. Crop Prot. *26*(12), 1733-1746.

Archambault, J. M., Bergeron, C. M., Cope, W. G., Richardson, R. J., Heilman, M. A., Corey III, J. E., Netherland, M.D., Heise, R. J., 2015. Sensitivity of freshwater molluscs to hydrilla-targeting herbicides: providing context for invasive aquatic weed control in diverse ecosystems. J. Freshwater Ecol. *30*(3), 335-348.

Bailey, G. W., White, J. L., 1964. Soil-pesticide relationships, adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticide bioactivity. J. Arg. Food Chem. *12*(4), 324-332.

Banks, P. A., Ketchersid, M. L., Merkle, M. G., 1979. The persistence of fluridone in various soils under field and controlled conditions. Weed Sci. *27*(6), 631-633.

Banks, P. A., Merkle, M. G., 1979. Field Evaluations of the Herbicidal Effects of Fluridone on Two Soils 1. Agron. J. *71*(5), 759-762.

Bear J., 1979. Hydraulics of Groundwater. New York: McGraw-Hill.

Beeton, A. M., 1958. Relationship between Secchi disc readings and light penetration in Lake Huron. T. Am. Fish. Soc. *87*(1), 73-79.

Bento, C. P., Yang, X., Gort, G., Xue, S., van Dam, R., Zomer, P., Mol, H.G., Ritsema, C.J., Geissen, V., 2016. Persistence of glyphosate and aminomethylphosphonic acid in loess soil under different combinations of temperature, soil moisture and light/darkness. Sci. Total Environ. 572, 301-311.

Berlioz-Barbier, A., Vauchez, A., Wiest, L., Baudot, R., Vulliet, E., Cren-Olivé, C., 2014. Multi-residue analysis of emerging pollutants in sediment using QuEChERS-based extraction followed by LC-MS/MS analysis. Anal. Bioanal. Chem. 406(4), 1259-1266.

Bruzzoniti, M. C., Checchini, L., De Carlo, R. M., Orlandini, S., Rivoira, L., Del Bubba, M., 2014. QuEChERS sample preparation for the determination of pesticides and other organic residues in environmental matrices: a critical review. Anal. Bioanal. Chem. 406(17), 4089-4116.

Bureau of Land Management (BLM), 2005. Fluridone Ecological Risk Assessment, Reno, Nevada

Castillo, M. D. P., Torstensson, L., 2007. Effect of biobed composition, moisture, and temperature on the degradation of pesticides. J. Arg. Food Chem. *55*(14), 5725-5733.

Cockreham, S. D., Netherland, M. D., 2000. Sonar use in California to manage exotic plants: hydrilla, Eurasian watermilfoil, and egeria. Proc. Calif. Weed Sci. Soc (Vol. 52, pp. 59-62).

Davis S.N., 1969. Porosity and permeability of natural materials in flow through porous materials. Academic Press, New York, 54-89

De Haan, H., 1993. Solar UV-light penetration and photodegradation of humic substances in peaty lake water. Limnol. Oceanogr. *38*(5), 1072-1076.

Dechoretz, N. (1989). Hydrilla Program in California: Current Status. In *Proceedings, 23rd Annual Meeting, Aquatic Plant Control Research Program: 14-17 November 1988, West Palm Beach, Florida* (p. 6). US Army Engineer Waterways Experiment Station.

Deverel S.J., Fujii R., 1988. Processes affecting the distribution of selenium in shallow groundwater of agricultural areas, western San Joaquin Valley, California. *Water Resources Research*, *24*(4), 516-524.

Domenico PA, Schwartz F.W., 1998. Physical and chemical hydrogeology (Vol. 506). New York: Wiley.

Doran, J. W., Zeiss, M. R., 2000. Soil health and sustainability: managing the biotic component of soil quality. Appl. Soil Ecol. 15(1), 3-11.

Fairchild, J., 2011. Structural and functional effects of herbicides on non-target organisms in aquatic ecosystems with an emphasis on atrazine. Herbicides and environment. (pp. 396-400) InTech.

Felsot, A. S., Shelton, D. R., 1993. Enhanced biodegradation of soil pesticides: interactions between physicochemical processes and microbial ecology. Sorption and degradation of pesticides and organic chemicals in soil, (sorptionanddegr), 227-251.

Flury M., 1996. Experimental evidence of transport of pesticides through field soils—a review. J Environmental Quality, *25*(1), 25-45.

Fox A.M., Haller W.T., Shilling D.G., 1996. Hydrilla control with split treatments of fluridone in Lake Harris, Florida. Management and Ecology of Freshwater Plants (pp. 235-239). Springer, Dordrecht.

Gan, J., Papiernik, S. K., Yates, S. R., Jury, W. A., 1999. Temperature and moisture effects on fumigant degradation in soil. J. Environ. Qual. 28(5), 1436-1441.

Garbin, J. R., Milori, D. M., Simoes, M. L., Da Silva, W. T., Neto, L. M., 2007. Influence of humic substances on the photolysis of aqueous pesticide residues. Chemosphere. *66*(9), 1692-1698.

Gauthier, E., Nikolić, M., Truss, R., Laycock, B., Halley, P., 2015. Effect of soil environment on the photo-degradation of polyethylene films. J. Appl. Poly. Sci. *132*(39).

Gauthier, E., Nikolić, M., Truss, R., Laycock, B., Halley, P., 2015. Effect of soil environment on the photo-degradation of polyethylene films. J. Appl. Poly. Sci. 132(39).

Gilliom R.J., 2007. Pesticides in US streams and groundwater.

Hamelink J.L., Buckler D.R., Mayer F.L., Palawski D.U., Sanders H.O., 1986. Toxicity of fluridone to aquatic invertebrates and fish. Environ Toxicol, *5*(1), 87-94.

Ingraham, J. L., Bailey, G. F., 1959. Comparative study of effect of temperature on metabolism of psychrophilic and mesophilic bacteria. J. Bacteriol. *77*(5), 609.

Jacob AP, Culver DA, Lanno RP, Voigt A, 2016. Ecological impacts of fluridone and copper sulphate in catfish aquaculture ponds. Environ. Toxicol. 35(5), 1183-1194.

Jin, J., Kurobe, T., Ramírez-Duarte, W. F., Bolotaolo, M. B., Lam, C. H., Pandey, P. K., Hung, T.C., Stillway, M.E., Zweig, L., Caudill, J., Lin, L., 2018. Sub-lethal effects of herbicides penoxsulam, imazamox, fluridone and glyphosate on Delta Smelt (Hypomesus transpacificus). Aquat. Toxicol. 197, 79-88.

Langeland KA, 1996. Hydrilla verticillata (LF) Royle (Hydrocharitaceae), The Perfect Aquatic Weed. Castanea, 293-304.

Langeland, K.A. and Pesacreta, G.J., 1986. Management program for hydrilla (a monoecious strain) in North Carolina. Water Resources Research Institute of the University of North Carolina.

Lin, J., Xie, L., Pietrafesa, L. J., Shen, J., Mallin, M. A., Durako, M. J., 2006. Dissolved oxygen stratification in two micro-tidal partially-mixed estuaries. Estuar. Coast. Shelf S. 70(3), 423-437.

Lloyd, J., Taylor, J. A., 1994. On the temperature dependence of soil respiration. Funct. Ecol. 315-323.

Lund-HØie, K., Friestad, H. O., 1986. Photodegradation of the herbicide glyphosate in water. B. Environ. Contam. Tox. *36*(1), 723-729.

MacDonald, G. E., Hailer, W. T., Shilling, D. G., 1996. UV-B filtration to reduce photolysis of Fluridone in experimental tanks. J Aquat. Plant Manage. *34*, 78-80.

Marquis, L. Y., Comes, R. D., Yang, C. P., 1982. Degradation of fluridone in submersed soils under controlled laboratory conditions. Pestic. Biochem. Phys. 17(1), 68-75.

Masiá, A., Vásquez, K., Campo, J., Picó, Y., 2015. Assessment of two extraction methods to determine pesticides in soils, sediments and sludges. Application to the Túria River Basin. J. Chromatography-A. 1378, 19-31.

McCloskey WB, Bayer DE, 1987. Thermodynamics of Fluridone Adsorption and Desorption on Three California Soils 1. Soil Sci. Soc. Am. J 51(3), 605-612.

Mossler, M. A., Shilling, D. G., Haller, W. T., 1989. Photolytic Degradation of Fluridone. Ecology *55*, 188-194.

Muir DCG, Grift NP, Blouw AP, Lockhart WL, 1980 Persistence of fluridone in small ponds. J Environ. Qual. 9, 151

Muir, D. C., Grift, N. P., 1982. Fate of fluridone in sediment and water in laboratory and field experiments. J. Arg. Food Chem. *30*(2), 238-244.

Netherland, M. D., Getsinger, K. D., 1995. Laboratory evaluation of threshold Fluridone concentrations under static conditions for controlling hydrilla and Eurasian watermilfoil. J Aquat. Plant Manage. *33*, 33-36.

Netherland, M. D., Getsinger, K. D., Skogerboe, J. D., 1997. Mesocosm evaluation of the species-selective potential of Fluridone. J Aquat. Plant Manage. *35*, 41-50.

Netherland, M. D., Jones, D., 2015. Fluridone-resistant hydrilla (Hydrilla verticillata) is still dominant in the kissimmee chain of lakes, FL. Invas. Plant Sci. Mana. *8*(2), 212-218

Nowell LH, Capel PD, Dileanis PD, 1999. Pesticides in stream sediment and aquatic biota: distribution, trends, and governing factors. CRC Press.

Ogata, A, Banks, R. B., 1961. A solution of the differential equation of longitudinal dispersion in porous media. Profl. Paper No. 411- A, U.S. Geological Survey, Washington, D.C

Orellana-García, F., Álvarez, M. A., López-Ramón, M. V., Rivera-Utrilla, J., Sánchez-Polo, M., 2015. Effect of HO, SO4− and CO3−/HCO3 radicals on the photodegradation of the herbicide amitrole by UV radiation in aqueous solution. Chem. Eng. J. *267*, 182-190.

Pauli Virtanen, Ralf Gommers, Travis E. Oliphant, Matt Haberland, Tyler Reddy, David Cournapeau, Evgeni Burovski, Pearu Peterson, Warren Weckesser, Jonathan Bright, Stéfan J. van der Walt, Matthew Brett, Joshua Wilson, K. Jarrod Millman, Nikolay Mayorov, Andrew R. J. Nelson, Eric Jones, Robert Kern, Eric Larson, CJ Carey, İlhan Polat, Yu Feng, Eric W. Moore, Jake VanderPlas, Denis Laxalde, Josef Perktold, Robert Cimrman, Ian Henriksen, E.A. Quintero, Charles R Harris, Anne M. Archibald, Antônio H. Ribeiro, Fabian Pedregosa, Paul van Mulbregt, and SciPy 1.0 Contributors, 2020. SciPy 1.0: Fundamental Algorithms for Scientific Computing in Python. Nature Methods, in press.

Parsons, J. K., Couto, A., Hamel, K. S., Marx, G. E., 2009. Effect of Fluridone on macrophytes and fish in a coastal Washington lake. J Aquat. Plant Manage. *47*, 31-40.

Posey MH, Wigand C, Stevenson JC, 1993. Effects of an introduced aquatic plant, Hydrilla verticillata, on benthic communities in the upper Chesapeake Bay. Estuar. Coast Shelf Sci 37(5), 539-555.

Saunders, D. G., Mosier, J. W., 1983. Photolysis of the aquatic herbicide Fluridone in aqueous solution. J. Arg. Food Chem. *31*(2), 237-241.

Schroeder, J., Banks, P. A., 1986. Persistence and activity of norflurazon and Fluridone in five Georgia soils under controlled conditions. Weed Sci. *34*(4), 599-606.

Schwartz FW, Domenico PA, 1990. Physical and chemical hydrogeology. John Wiley.

Shea, P.J., Weber, J.B., 1983. Effect of soil pH on fluridone activity and persistence as determined by chlorophyll measurements. Weed Sci., 31(3), pp.347-350.

Shrikant, B., Khambete, A.K., 2014. Photolysis: Case studies for Organophosphate Pesticide Treatment. IRJET

Si, Y., Zhou, J., Chen, H., Zhou, D., Yue, Y., 2004. Effects of humic substances on photodegradation of bensulfuron-methyl on dry soil surfaces. Chemosphere. *56*(10), 967-972.

Siemering G, 2004. Aquatic Pesticide Monitoring Program Phase 2 (2003) Monitoring Project Report. San Francisco Estuary Institute.

Siemering, G. S., Hayworth, J. D., Greenfield, B. K., 2008. Assessment of potential aquatic herbicide impacts to California aquatic ecosystems. Arch. Environ. Con. Tox. *55*(3), 415-431.

Tian, J., Philpot, W. D., 2015. Relationship between surface soil water content, evaporation rate, and water absorption band depths in SWIR reflectance spectra. Remote Sens. Environ. *169*, 280-289.

United States Environmental Protection Agency, 2017. Introduction to Pesticide Labels. Retrieved February 25, 2019, from https://www.epa.gov/pesticide-labels/introduction-pesticide-labels

United States Environmental Protection Agency, 2018. Summary of the Clean Water Act. Retrieved February 25, 2019, from https://www.epa.gov/laws-regulations/summary-clean-water-act

Vanderborght J, Vereecken H, 2007. Review of dispersivities for transport modeling in soils. J Vadose Zone, *6*(1), 29-52.

Vassios JD, 2010. Evaluation of herbicides for control of Eurasian watermilfoil and sago pondweed (Doctoral dissertation, Colorado State University Libraries).

Vinolas, L. C., Vallejo, V. R., Jones, D. L., 2001. Control of amino acid mineralization and microbial metabolism by temperature. Soil Biol. Biochem. 33(7-8), 1137-1140.

Vischetti, C., Monaci, E., Cardinali, A., Casucci, C., Perucci, P., 2008. The effect of initial concentration, co-application and repeated applications on pesticide degradation in a biobed mixture. Chemosphere, 72(11), 1739-1743.

Vozza, G. M., 2013. Riverbed Filtration Clogging at Wohler on the Russian River, Sonoma County, California.

Wang H.F., Anderson M.P., 1995. Introduction to groundwater modeling: finite difference and finite element methods. Academic Press.

Weber, J. B., Wilkerson, G. G., & Reinhardt, C. F. (2004). Calculating pesticide sorption coefficients (Kd) using selected soil properties. Chemosphere, 55(2), 157-166.

West, S. D., Burger, R. O., Poole, G. M., Mowrey, D. H., 1983. Bioconcentration and field dissipation of the aquatic herbicide Fluridone and its degradation products in aquatic environments. J. Arg. Food Chem. *31*(3), 579-585.

West, S. D., Day Jr, E. W., Burger, R. O., 1979. Dissipation of the experimental aquatic herbicide fluridone from lakes and ponds. J. Arg. Food Chem. *27*(5), 1067-1072.

West, S. D., Parka, S. J., 1981. Determination of the aquatic herbicide fluridone in water and hydrosoil: Effect of application method on dissipation. J. Arg. Food Chem. *29*(2), 223-226.

Wilson A.M., Gardner L.R., 2006. Tidally driven groundwater flow and solute exchange in a marsh: numerical simulations. Water Resources Research, *42*(1).

Yi A.S., Francis B.M., Jarrell W.M., Soucek D.J., 2011. Toxicological effects of the aquatic herbicide, fluridone, on male water mites (Hydrachnidiae: Arrenurus: Megaluracarus). Ecotox., 20(1), 81-87.

Yu, Y. L., Wu, X. M., Li, S. N., Fang, H., Zhan, H. Y., Yu, J. Q., 2006. An exploration of the relationship between adsorption and bioavailability of pesticides in soil to earthworm. Environ. Pollut. *141*(3), 428-433.

Zhang, Y., Hubbard, S., Finsterle, S., 2011. Factors governing sustainable groundwater pumping near a river. Groundwater, *49*(3), 432-444.