

**Hydroxyl Radical Production in Old Woman Creek National
Estuarine Reserve**

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INTRODUCTION

Purpose of Research

The goal of this research project was to quantify the amount of hydroxyl radical present under different photosensitizing conditions in Old Woman Creek National Estuarine Reserve (OWC). Hydroxyl radical is a critical reactive species responsible for the degradation of organic compounds. The experiments examined the effects of dissolved organic matter (DOM), nitrate, and iron (III) on the hydroxyl radical steady state concentration. The second goal of this research project was to kinetically model the degradation of ibuprofen in OWC to determine the role of hydroxyl radical. The second-order reaction rate constant between hydroxyl radical and ibuprofen is known and as a result, the persistence of ibuprofen in wetlands can be predicted under different photosensitizing conditions in OWC. The data collected in this research will be of value to other scientists conducting photochemical research in surface waters.

Overview

Wastewater treatment facilities in the U.S. are limited in their ability to remove pharmaceutical compounds and hormones (1). As a result, many of these substances persist in the environment at low but measurable levels. In a survey of 139 streams sampled by the U.S. Geological Survey from 1999-2000, a median of seven organic wastewater contaminants (WWCs) were detected in a given water sample (2). Many of these WWCs do not have maximum contaminant levels (MCLs) established by the EPA. Ibuprofen, a frequently used over-the-counter medication, was detected in 9.5% of streams sampled and does not have an established MCL. Limited information is available as to how synthetic organic compounds degrade in the environment or how they are affecting aquatic and human health. A study by

Halling-Sorensen, et. al., (1998) concluded with respect to pharmaceutical fate in the environment that “the knowledge is practically zero” (1).

Wetlands receive many WWCs from municipal sources as well as unregulated septic systems in rural households. Photochemical degradation of organic compounds is potentially an important degradative pathway for WWCs in wetlands because the shallow depth of water allows for significant sunlight penetration (3). Photolytic degradation of a compound can occur *directly* by that compound’s absorption of sunlight. Photolytic degradation can also occur *indirectly* when photosensitizers such as dissolved organic matter (DOM), iron, and nitrate in the wetland absorb sunlight and create free radicals that react readily with the target compound. This latter pathway is particularly important for compounds that cannot absorb sunlight. Miller and Chin (2002, 2005) have demonstrated that photochemical degradation of the herbicide alachlor and the pesticide carbaryl can occur by indirect photolysis (3, 4). Cawley (2005) has also shown that indirect photodegradation of the organic compounds 2,4,6-trimethylphenol, atrazine and metolachlor can occur in wetland waters (5).

Background on Hydroxyl Radical

The hydroxyl radical (OH•) is one of the most important reactive species created by indirect photolytic processes. The hydroxyl radical can rapidly oxidize many organic compounds in the environment, thus its presence is highly significant to the fate of environmental organic pollutants. Hydroxyl radical production is known to occur by the direct photolysis of DOM (6, 7), photolysis of nitrite and nitrate (8, 9), and the photolysis of iron (III) at pH less than 5.6 (10). In this study, the impact of DOM, nitrate, and iron (III) on the production of hydroxyl radical in OWC waters was examined.

The work of Mopper and Zhou has demonstrated that DOM present in seawaters produces hydroxyl radical under direct photolysis (7). The rate of hydroxyl radical production changes dramatically with the composition of the DOM, whereby the net hydroxyl radical concentration, or the concentration at steady state ($[\text{OH}\cdot]_{\text{ss}}$), must be determined in DOM from the source water in order to accurately characterize the photolytic pathways of a contaminant in that water.

Irradiation of nitrate (NO_3^-) at wavelengths greater than 280 nm results in two photolytic pathways (8):

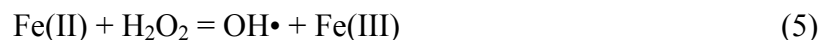


The second pathway produces hydroxyl radical, as identified by Equation 3. Nitrite also reacts to produce hydroxyl radical, but it is a very efficient hydroxyl radical scavenger ($k=1.0 \times 10^{10} \text{ s}^{-1}$) (11). Net production of hydroxyl radical due to nitrite is negligible. At high concentrations of nitrate, an accumulation of nitrite from photolysis of nitrate will have a noticeable scavenging effect on the hydroxyl radical concentration (8).

When Fe(III) is present in a natural system, it is photochemically reduced to Fe(II),



where L_n is a ligand. Iron (II) reacts readily with hydrogen peroxide to create hydroxyl radical.



Hydrogen peroxide is abundant in natural waters and is formed when superoxide disproportionates (12). Superoxide is produced by the reduction of O_2 by photo-excited DOM.

Photochemical reactions involving the oxidation of organic substances by Fe(II) and hydrogen peroxide are referred to as photo-Fenton processes (10).

DOM, nitrate, and iron are commonly found in wetlands. DOM is due to the presence of naturally occurring organic debris and microbial waste, nitrate is a common fertilizer component, and iron is present in municipal waste. As the three most photochemically-relevant components to hydroxyl radical production, experiments were conducted in order to examine the individual effects of DOM, nitrate, and iron.

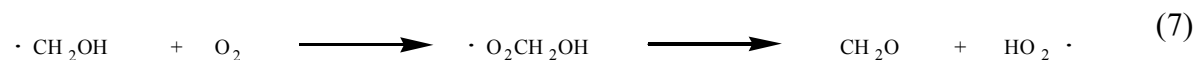
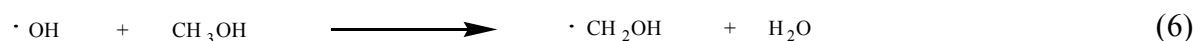
MATERIALS AND METHODS

Collection and Preparation of Sample Waters

The field site used in this project is Old Woman Creek National Estuarine Reserve (OWC), a NOAA-operated natural wetland that feeds into Lake Erie in Northern Ohio. Two types of natural water solutions were used in experiments: unmodified whole water and Milli-Q spiked with Old Woman Creek XAD-8 filtered fulvic acid. Whole water was collected from the inlet of the wetland in June 2006 and stored unacidified at 4°C in a cooler. This water was used without modification for experiments conducted in whole water. In September 2006, 500 liters of OWC water was collected. Fulvic acid, a DOM isolate, was separated from the whole water using an XAD-8 sorption process developed by Aiken, et al. (13). The whole water was filtered using a Balston filter apparatus that removed particles to 0.5µm. The filtered water was acidified between pH 2.5 and 3 and stored in a cooler at 4°C. The Balston-filtered water was passed at 50 mL/min through a 2 liter column of clean XAD-8 resin until the absorbance of the effluent reached 50% of the absorbance of the influent. The column was back eluted with a sodium hydroxide solution and the concentrated retentate was stored and reconcentrated one more time. The reconcentrated retentate was freeze-dried and yielded 1.5 grams of fulvic acid. Fulvic acid is a yellow-brown, hydrophilic, low density solid. Fulvic acid solutions of 8 and 16 mg/L were prepared in Milli-Q water to regenerate the sample waters. Exact levels of dissolved organic carbon (DOC) were measured using a Total Organic Carbon Analyzer. Sodium bicarbonate, potassium nitrate, and Iron (III) chloride were also added to the sample waters selectively to simulate the desired levels of photosensitizer for each experiment.

Experimental Procedure

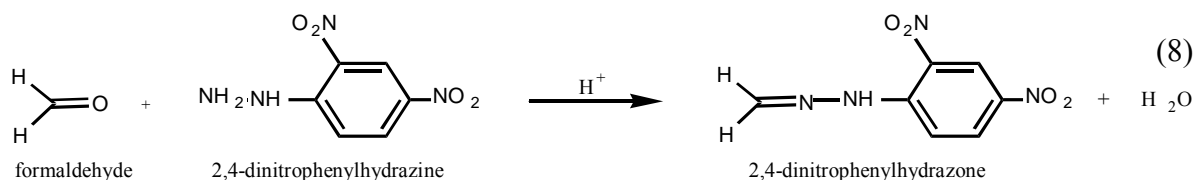
The production of formaldehyde by the reaction of OH• with methanol was used to quantify hydroxyl radical production in sample waters (7). Solutions of five methanol concentrations that ranged between 0 mM and 15 mM were prepared in sample waters with 99.9% pure methanol. Methanol reacts with hydroxyl radical to produce formaldehyde:



Whole water sample solutions were filled with zero headspace into 7 mL borosilicate glass tubes. Eight tubes were filled per methanol concentration: time points T₀ through T₆ and a dark control. Fulvic acid sample solutions were filled into 6 mL quartz glass tubes with zero headspace and clamped shut. Four tubes were filled per methanol concentration: time points T₀ through T₃. Every tube, borosilicate or quartz, was covered with Teflon to prevent the evolution of formaldehyde gas.

All methanol concentrations were irradiated for 3 hours in a Suntest CPS+ Solar Simulator. A tube from each methanol concentration was removed every half hour for the whole water solutions and every hour for the fulvic acid solutions. The number of time points was determined by the number of tubes the Suntest could hold: the Suntest can hold 32 borosilicate tubes and 18 quartz tubes.

The irradiated solutions were derivatized with 2,4-dinitrophenylhydrazine (DNPH) to produce the corresponding adduct, 2,4-dinitrophenylhydrazone:



A derivitization reagent was used in these experiments because formaldehyde cannot be assayed in a High Performance Liquid Chromatography (HPLC) instrument due to its high volatility. Three mL of each irradiated sample was transferred to a 4 mL HPLC brown vial. 50 μ L of saturated DNPH in 0.5 M HCl was spiked into each solution. After derivitization, solutions sat for an hour before analysis.

Analytical Methods

All solutions were analyzed on a Waters High Pressure Liquid Chromatography (HPLC) analytical instrument. Solutions were sampled automatically from vials on an autosampler and run isocratically through a UV-vis detector set to 360 nm. The mobile phase was 60% water/40% acetonitrile and ran at a flow rate of 1 mL/min. Separation was achieved using a C-18 Restek column. Breeze software was used to record the absorption spectrum. The DNPH peak separated around 2.5 minutes and the DNPH-adduct peak separated around 6 minutes. The adduct peak was always several orders of magnitude smaller than the DNPH peak. No other major peaks were observed at 360 nm.

Recrystallization of DNPH from Acetonitrile

The derivitization reagent, 2,4-dinitrophenylhydrazine, was purchased from Sigma Aldrich as a solid. The reagent is a shiny, red crystalline solid. The DNPH is originally 97% pure and it must be recrystallized to remove impurities. A recrystallization apparatus was constructed in a well-ventilated hood, as shown in Figure 1. A 500 mL roundbottom flask was set up in a Variac heating mantle. A condensing column was attached to the round bottom, and the cooling water (25°C) in and out tubing was connected to the condensing column. Tubing connected the outlet of the condensing column to a gas trap. The gas trap bubbled into a flask of

6 M NaOH. The gas trap and NaOH container prevented the evolution of cyanide gas into the room, which is produced during heating of DNPH.

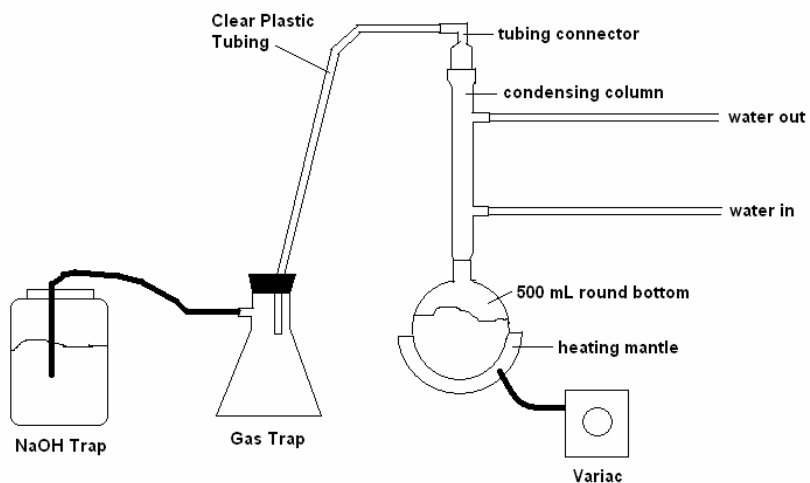


Figure 1: DNPH Recrystallization Apparatus

In the round bottom flask, a reddish-yellow solution of 3.5 g DNPH and 200 mL acetonitrile was prepared. Most of the solid did not dissolve at room temperature. The solution was heated to a gentle boil at a Variac setting of about 70-75 °C. Boiling began at about 75°C and the solution was left on a low boil for an hour. All the DNPH crystals dissolved during boiling. The solution was transferred to a beaker and placed on a hot plate where it was maintained at a temperature between 40°C and 60°C for 1 hour while acetonitrile boiled off. The solution was transferred to a new round bottom flask and sealed with Teflon tape. The solution cooled in a refrigerator overnight. The next day, red crystals had formed in the solution. The crystals were isolated using a Buechner funnel vacuum filtration and rinsed with 20 mL of room temperature acetonitrile. The crystals were transferred to a 400 mL beaker and 200 mL of acetonitrile was added. The beaker was covered with a watch glass and heated to a boil. After

several minutes of boiling, the temperature was reduced to 55°C and maintained between 50 and 60°C until only 50 mL of acetonitrile remained. Periodically, the watch glass was removed to release vapors. It took approximately 3 hours for the acetonitrile to boil down to 25 mL. The beaker was removed from heat and within several minutes, the crystals precipitated out of solution as the temperature dropped. The crystals were vacuum-filtered with a Buechner funnel and rinsed twice with room temperature, reagent-grade acetonitrile. The crystals were stored in 50 mL of acetonitrile in the freezer. Many crystals remained undissolved in the vial. The supersaturated DNPH solution was used for the duration of hydroxyl steady state experiments.

Preparation of Formaldehyde Standards

Solutions of formaldehyde were prepared in sample water to create a standard calibration curve. Standards were prepared in sample water rather than Milli-Q because a background concentration of aldehyde exists in the sample water and is susceptible to derivitization by DNPH. The concentrations of formaldehyde observed by photolysis are on the order of 0.5 to 5 μM . Six formaldehyde standards were prepared at concentrations of 0, 0.5, 1, 5, 10, and 15 μM . Formaldehyde was available in the lab at 37.6% formaldehyde by mass, the balance containing methanol and inerts. All standards were prepared immediately before use because volatility of the formaldehyde prevented advance preparation and storage. Once the solutions were prepared, 3.5 mL of each were transferred to 4 mL HPLC brown glass vials. A stock vial of DNPH in 0.5M HCl was prepared from the supersaturated DNPH solution. Each formaldehyde standard was spiked with 50 μL of the acidified DNPH stock. Vials sat for an hour before analysis in the HPLC.

RESULTS AND DISCUSSION

Experiments Performed

A summary of the experiments conducted and their dates of occurrence can be found in Table 1.

Table 1: Summary of OH• Experiments

Experiment	Date of Experiment	Components of Sample Water			
		[DOC] (mg/L)	[NO ₃ ⁻] (μM)	[Fe(III)] (μM)	[NaHCO ₃] (mM)
Whole Water	10/25/2006	2.8	135	unknown	unknown
Whole Water Replicate	1/21/2006	2.8	135	unknown	unknown
Fulvic Acid Solutions					
Low DOC	4/2/2007	4.68	-	-	-
High DOC	4/25/2007	6.10	-	-	2.41
Low DOC, Iron	4/20/2007	3.31	-	20.9	2.46
High DOC, Iron	5/5/2007	7.45	-	20.2	2.39
Low DOC, High Nitrate	4/22/2007	3.86	454	-	2.43
High DOC, High Nitrate	5/4/2007	7.45	430	-	2.42

Calculation of OH•

A calibration curve was prepared from the formaldehyde standards' absorbance peak areas. From this curve, concentrations of formaldehyde were determined for each irradiated sample. A plot of concentration of formaldehyde as a function of time was prepared for each methanol concentration (Figure 2). Linear production rates were observed and linear fits were constructed for each methanol concentration. The production rate of formaldehyde ($d[F]/dt$) was determined from the slope of each line. The reaction of hydroxyl radical with methanol (MeOH) exhibits second order kinetics:

$$d[F]/dt = k_{\text{MeOH}}[\text{OH}\cdot][\text{MeOH}] \quad (9)$$

where k_{MeOH} is the second order rate constant. The photolysis of a 15 mM methanol solution resulted in a formaldehyde production rate of 0.8384 M/hr (Figure 3).

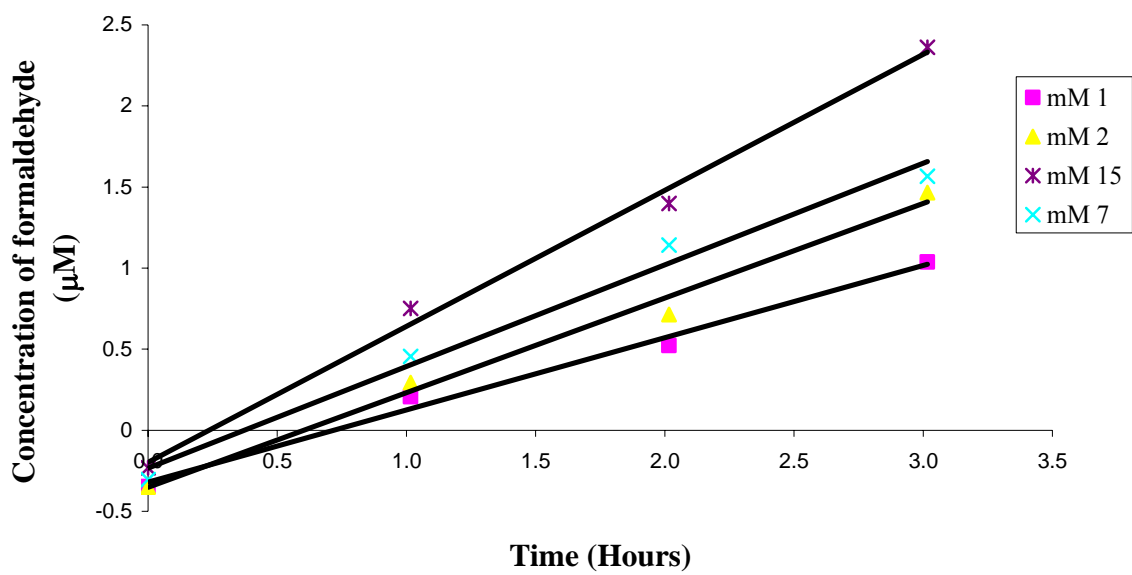


Figure 2: Formaldehyde production under various methanol concentrations in low DOC water (4-2-2007) using OWC FA

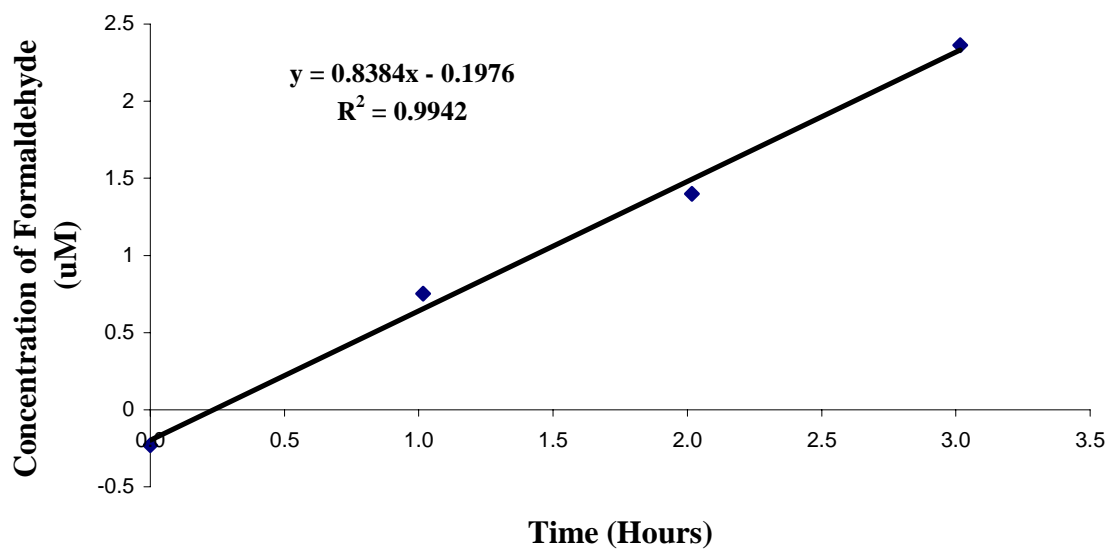


Figure 3: Formaldehyde Production for 15 mM methanol in low DOC water (4-2-2007) using OWC FA

Hydroxyl radical is consumed by both methanol and other scavengers (os) present in the natural water. The balance on hydroxyl radical is:

$$d[\text{OH}\cdot]/dt = R_{\text{OH}} - k_{\text{MeOH}}[\text{OH}\cdot][\text{MeOH}] - k_{\text{os}}[\text{OH}\cdot][\text{OS}] = 0 \quad (10)$$

where $d[\text{OH}\cdot]/dt$ is the net production rate of hydroxyl radical, R_{OH} is the production rate of hydroxyl radical, and k_{os} is the second order rate constant between hydroxyl radical and all other hydroxyl radical scavengers.

Once the formaldehyde production rates were calculated, a plot of $d[\text{F}]/dt$ vs. $[\text{MeOH}]$ was prepared, as in Figure 4. As the concentration of methanol increases in the system, it becomes the dominant scavenger. The production rates of formaldehyde asymptotically increase towards the production rate of hydroxyl radical. The production rate of hydroxyl radical, or R_{OH} , shown by the data in Figure 4 is about 0.85 M/s.

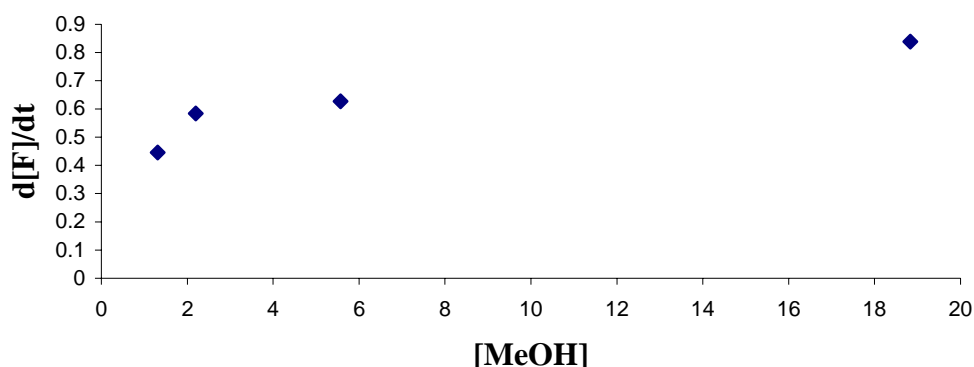


Figure 4: Plot of $d[\text{F}]/dt$ vs. $[\text{MeOH}]$ in low DOC water (4-2-2007) using OWC FA

The inverse of the previous plot, $1/d[\text{F}]/dt$ vs. $1/[\text{MeOH}]$ provides the critical information for determining $[\text{OH}\cdot]_{\text{ss}}$. The plot in Figure 5 is the inverse of the plot in Figure 4. The equation of the line fit to the inverse data in Figure 5 is:

$$1/d[\text{F}]/dt = 1/R_{\text{OH}} + (k_{\text{os}}[\text{OS}]/k_{\text{meoh}} R_{\text{OH}}) \times (1/[\text{MeOH}]) \quad (11)$$

The slope of this line can be used to determine $k_{os}[OS]$ for the natural system, which is $0.8384 \text{ hr}\cdot\text{mM}/\mu\text{M}$ for the data in Figure 5. $[OH\bullet]_{ss}$ is calculated by Equation 12 for a system without methanol:

$$[OH\bullet]_{ss} = R_{OH}/(k_{os}[OS]) \quad (12)$$

$[OH\bullet]_{ss}$ for the data in Figures 2 through 5 is $2.13 \times 10^{-16} \text{ M}$.

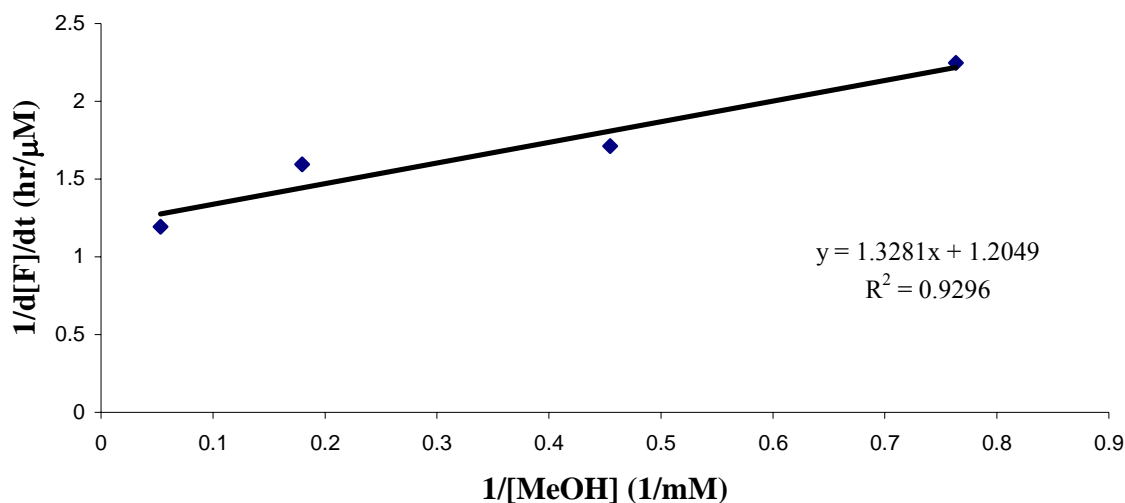


Figure 5: Plot of $1/d[F]/dt$ vs. $1/[MeOH]$ in low DOC water (4-2-2007) using OWC FA

Calculation of Error

All raw data were input into JMP software for error processing. A linear fit was applied to the inverse formaldehyde production rates and a standard error was calculated on the slope and intercept (hydroxyl radical production rate) of the line. The error on the slope was propagated into the calculation of $[OH\bullet]_{ss}$ using a formula based on differentials, where $delOH$ is the error associated with $[OH\bullet]_{ss}$:

$$delOH := \sqrt{\left(\frac{\delta OH_{ss}}{\delta slope}\right)^2 \cdot slope_{error}^2} \quad (13)$$

The hydroxyl radical production rate is not used to calculate $[\text{OH}\cdot]_{\text{ss}}$, so its associated error was not propagated.

Observations and Problems Encountered in Data Collection

Many other data sets were excluded from this final collection due to errors in experimental preparation. In early experiments, formaldehyde vapor leaked from borosilicate tubes during photolysis. The addition of Teflon septa completely ameliorated this problem. Calibration standards were originally prepared a day in advance and in Milli-Q. Formaldehyde volatilized out of the volumetric flasks when sitting overnight. Better linearity in standard curves was achieved with standards prepared immediately before use and in sample waters. Methanol solutions were also prepared immediately before use to prevent volatilization. Whole water solutions produced steady state numbers with less associated error than did fulvic acid solutions, as demonstrated in Table 2.

Table 2: Associated Error of Each $[\text{OH}\cdot]_{\text{ss}}$

Experiment	Error (x 10 ¹⁶)
Whole Water	0.04
Whole Water (replicate)	0.3
Fulvic Acid Solutions	
Low DOC	0.41
High DOC	0.66
Low DOC, Iron	-
High DOC, Iron	1.3
Low DOC, Nitrate	1.5
High DOC, Nitrate	5.0

The linear fit to the inverse formaldehyde production rates vs. inverse methanol concentration (e.g. Figure 5) yielded R^2 values of 0.997 and 0.960 in the whole water experiments; in the fulvic acid experiments, the R^2 on these fits ranged from 0.83 to 0.935.

In multiple fulvic acid experiments, one of the methanol concentrations would yield a formaldehyde production rate that deviated greatly from the linearity of the rest of the production

rates. From the low DOC, 20 μM Iron (III) solution, the inverse formaldehyde production rates are plotted in Figure 6. The methanol concentration of 3.39 mM does not follow the linear trend established by the other data points. In Figure 7, this data point is excluded and a perfect linear fit was achieved.

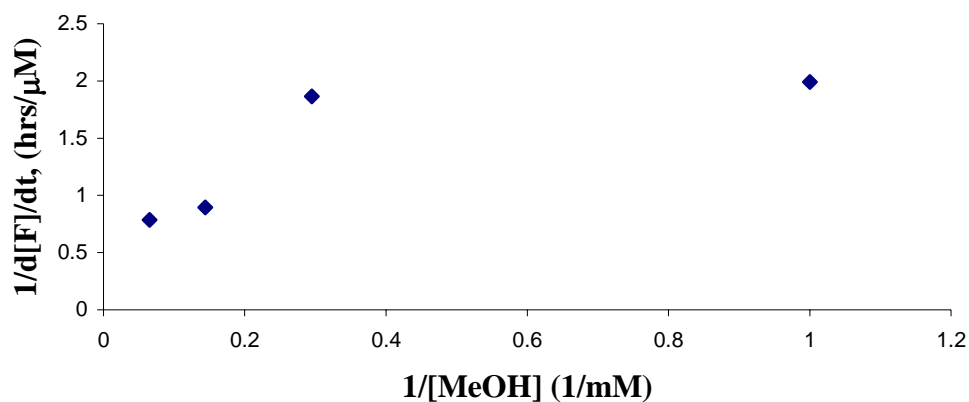


Figure 6: Irregular Data from the low DOC, 20 μM Iron (III) solution experiment (4-20-2007)

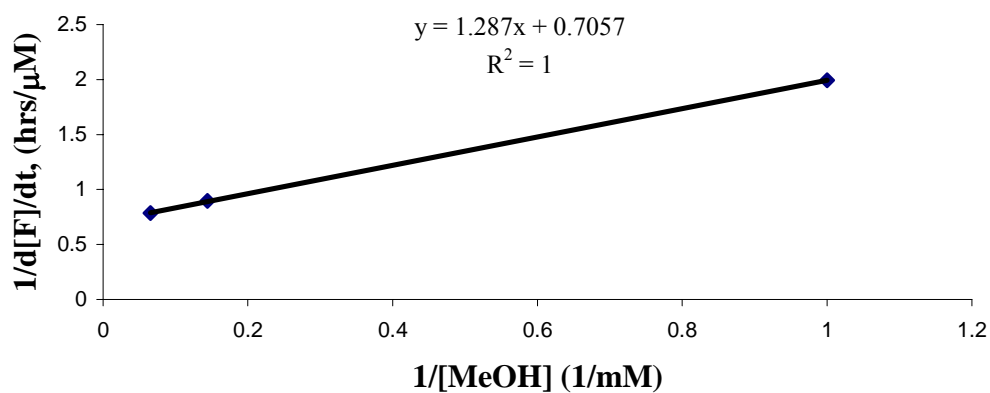


Figure 7: Data from the low DOC, μM Iron (III) solution experiment (4-20-2007) with 3.39 M MeOH excluded

This type of outlier never appeared in the whole water experimental data and may be the result of a non-homogeneously mixed stock fulvic acid solution. Less fulvic acid might have ended up in one of the methanol vials and produced a non-representative result. Overnight mixing of the fulvic acid stock solution helped alleviate this problem but did not fix it entirely. From the irregularities observed with fulvic acid solutions, hydroxyl steady state concentrations might be more reliable when measured in whole water solutions.

The Effect of Different Water Constituents

The $[\text{OH}\cdot]_{\text{ss}}$ values calculated from each experiment are displayed in Figure 8. $[\text{OH}\cdot]_{\text{ss}}$ ranges from 2×10^{-16} in 4.7 mg/L DOC FA to 1.5×10^{-15} in 7.5 mg/L DOC and 450 μM iron. Brezonik and Fulkerson-Brekken quantified $[\text{OH}\cdot]_{\text{ss}}$ values for five Minnesota waters under laboratory and natural conditions; their $[\text{OH}\cdot]_{\text{ss}}$ values ranged from 3.8×10^{-15} to 1.5×10^{-14} M under laboratory conditions using a medium-pressure quartz mercury vapor lamp and from 2.5×10^{-17} to 1.0×10^{-15} M for surface waters under natural sunlight conditions (14). All solutions were prepared in 0.143 to 1.43 mM nitrate. $[\text{OH}\cdot]_{\text{ss}}$ values are comparable between OWC FA solutions and Minnesota waters when nitrate levels and alkalinity are taken into account.

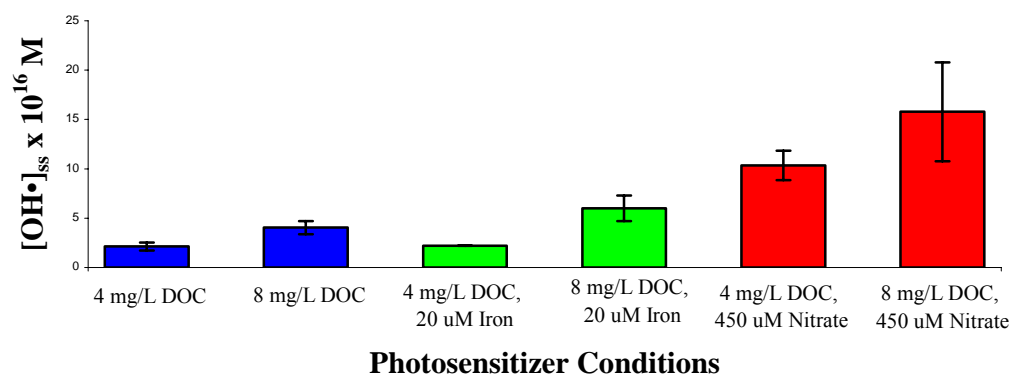


Figure 8: Summary of $[\text{OH}\cdot]_{\text{ss}}$ for Fulvic Acid Solutions Under Different Photosensitizer Conditions

The comparison of the effect of different photosensitizers is very straightforward. OWC fulvic acid solutions with no other constituents produce a measurable amount of hydroxyl radical. The amount of fulvic acid present in the water is directly related to the amount of hydroxyl radical produced. Comparing $[\text{OH}\cdot]_{\text{ss}}$ formed in high DOC and low DOC water, more hydroxyl radical is present when the DOC is higher. This relationship was observed under all conditions studied (FA, FA + Iron, FA + NO_3^-). Compared to the Brezonik study, the opposite trend was observed in Minnesota waters: $[\text{OH}\cdot]_{\text{ss}}$ is inversely related to $[\text{DOC}]$ (14). The authors state that the Minnesota waters' DOM has a net scavenging effect on hydroxyl radical whereas OWC waters have a net production effect on hydroxyl radical, as observed in this study. More experiments at other DOC levels could lead to the development of a mathematical model that relates $[\text{OH}\cdot]_{\text{ss}}$ to $[\text{DOC}]$, but there is not enough data in this data set to conclude an approximate mathematical relationship.

Iron is not a major contributor to $[\text{OH}\cdot]_{\text{ss}}$ in OWC wetland. At approximately 4 mg/L DOC, the addition of iron to the solution does not have a statistically significant effect on $[\text{OH}\cdot]_{\text{ss}}$. At approximately 7 mg/L DOC, the iron did increase $[\text{OH}\cdot]_{\text{ss}}$, but the result is not statistically different than the corresponding solution that lacks iron. Nitrate is the most important photosensitizer with regard to hydroxyl radical. The addition of 450 μM nitrate, a level typical in OWC after a major storm event, increases $[\text{OH}\cdot]_{\text{ss}}$ 3 to 5 times.

Comparison of Fulvic Acid Solution Results to Whole Water Results

An approximate comparison of $[\text{OH}\cdot]_{\text{ss}}$ can be made between fulvic acid solution and whole water solution to test the accuracy of sample water re-creation. In Figure 9, the DNPH method is only reproducible within 50 to 100% (personal communication with Dr. Chin); the replicate whole water solution yielded an $[\text{OH}\cdot]_{\text{ss}}$ value that is approximately 50% larger than the

first experiment. The reproducibility of the method itself thus should be factored into the comparison of fulvic acid solution to whole water. The fulvic acid solution in Figure 9 has the largest $[\text{OH}\cdot]_{\text{ss}}$, at about 2.1×10^{-16} M. Considering its DOC level is 1.5 times higher, a higher $[\text{OH}\cdot]_{\text{ss}}$ value would be expected. Additionally, the fulvic acid solution is unbuffered so it has less hydroxyl radical scavenging ability than the buffered whole water. The whole water has $135 \mu\text{M NO}_3^-$, so it has additional photosensitizer present in its composition that the fulvic acid solution does not possess. Overall, in light of the error bars, reproducibility of the DNPH method, and rough measures of comparison, the fulvic acid solution appears to be a reliable re-creation of whole water.

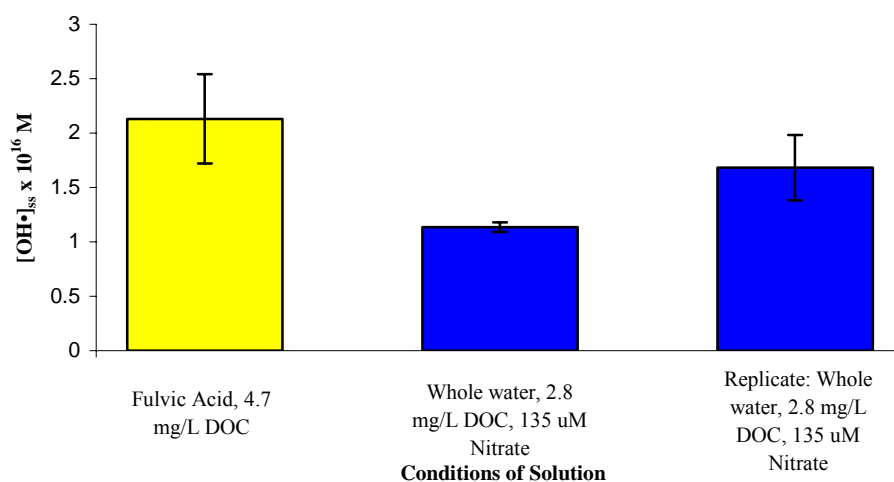


Figure 9: $[\text{OH}\cdot]_{\text{ss}}$ Comparison of Whole Water to Fulvic Acid Solution

Application of Results

The primary use of the hydroxyl radical steady state values under different photosensitizing conditions is to predict how quickly contaminants will degrade in the environment due to an indirect, hydroxyl radical-driven pathway. Hydroxyl radical reacts non-selectively with organic compounds by hydrogen abstraction or hydroxyl addition (14). Of

particular interest is the degradation of ibuprofen, a target contaminant that PhD candidate Laura Jacobs is investigating. Ibuprofen has the potential to degrade by direct photolysis, as identified by the blue photolysis data in Figure 10 (data courtesy of Laura Jacobs).

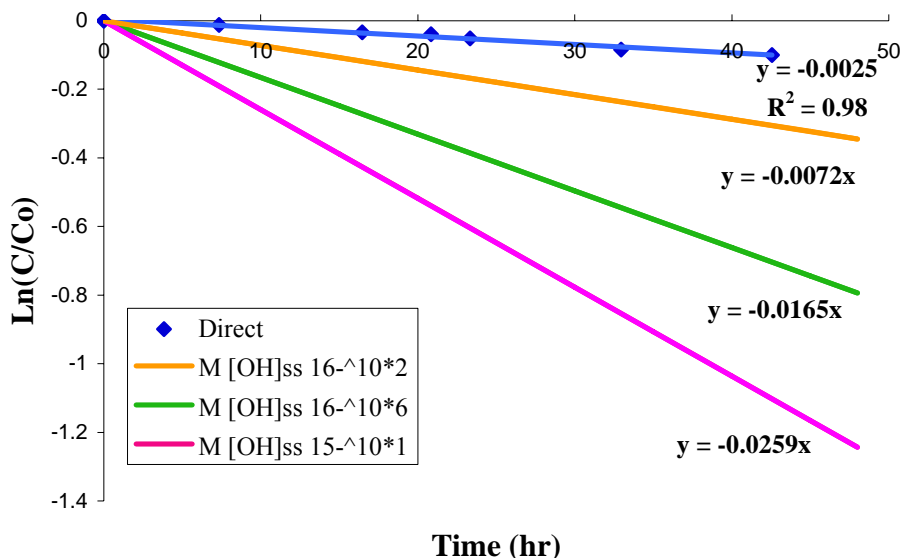


Figure 10: Modeling ibuprofen degradation: Ibuprofen photolytic degradation at different $[\text{OH}\cdot]_{\text{ss}}$

The degradation of ibuprofen is a function of direct and indirect photolytic processes:

$$d[\text{Ibu}]/dt = k_{\text{direct}} [\text{Ibu}] + k_{\text{indirect}} [\text{Ibu}]. \quad (14)$$

where $d[\text{Ibu}]/dt$ is the destruction rate of ibuprofen, k_{direct} is the direct breakdown rate of ibuprofen, k_{indirect} is the indirect breakdown rate of ibuprofen, and $[\text{Ibu}]$ is the concentration of ibuprofen. The indirect component comprises all reactions that degrade ibuprofen through other constituents in the water absorbing sunlight. The reaction rate of indirect photolysis can be broken down:

$$k_{\text{indirect}} = k_{\text{OH}\cdot 2\text{nd}} [\text{OH}\cdot]_{\text{ss}} + k_{\text{other2nd}} [\text{other}]_{\text{ss}} \quad (15)$$

where $k_{\text{OH}\cdot 2\text{nd}}$ is the second order rate constant of ibuprofen and hydroxyl radical and $k_{\text{other}2\text{nd}}$ is the second order rate constant of other radicals and ibuprofen. Ibuprofen has a reported second order rate constant ($k_{\text{OH}\cdot 2\text{nd}}$) of $6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ with $\text{OH}\cdot$ (15). Figure 10 shows how the degradation of ibuprofen increases due to different levels of hydroxyl radical present in the water. The orange, green, and pink lines are not actual data and do not consider other indirect photolytic reactions beyond hydroxyl radical. Increasing $[\text{OH}\cdot]_{\text{ss}}$ from $2 \times 10^{-16} \text{ M}$ to $10 \times 10^{-16} \text{ M}$ decreases ibuprofen's half life by 3.6 times.

For the degradation of ibuprofen in a FA solution, the contribution due to hydroxyl radical can be delineated when the corresponding value of $[\text{OH}\cdot]_{\text{ss}}$ is known. Figure 11 identifies the proportion of degradation of ibuprofen due to hydroxyl radical. Total degradation data for ibuprofen in an approximately 6 mg/L DOC OWC FA solution is provided by Laura Jacobs and is identified by the green data in Figure 11. Using the hydroxyl radical steady state value calculated for a 6 mg/L FA solution ($5.99 \times 10^{-16} \text{ M}$, 4-25-2007 data), the amount of degradation due to direct photolysis and indirect photolysis by hydroxyl radical is calculated and identified in Figure 11 by the pink line. The contribution due to hydroxyl radical nearly accounts for all indirect degradation in ibuprofen. The error associated with $[\text{OH}\cdot]_{\text{ss}}$ might overestimate its true contribution. Overall, hydroxyl radical is very important to the photolytic degradation of ibuprofen.

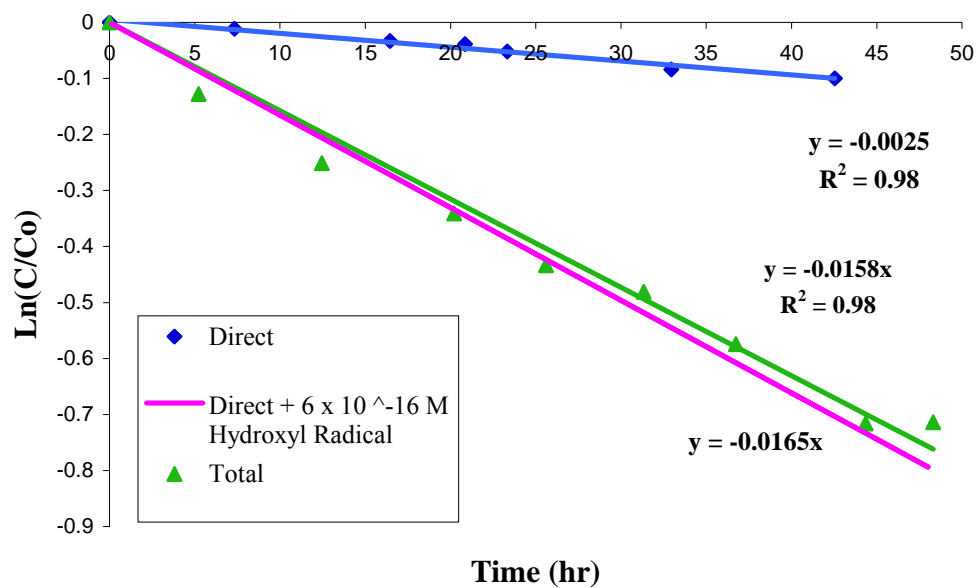


Figure 11: Contribution of Hydroxyl Radical to Degradation of Ibuprofen

CONCLUSIONS

The effects of the photosensitizers DOM, nitrate, and Iron (III) on the steady state concentration of hydroxyl radical in Old Woman Creek were examined in this study. DOM and nitrate influence $[\text{OH}\cdot]_{\text{ss}}$ while Iron (III) does not strongly influence $[\text{OH}\cdot]_{\text{ss}}$. Nitrate is the most important photosensitizer in this study: at a level of 450 μM , $[\text{OH}\cdot]_{\text{ss}}$ increases 3 to 5 times from the corresponding fulvic acid solution of the same $[\text{DOC}]$ without nitrate. OWC fulvic acid shows a net production effect with regard to hydroxyl radical. As $[\text{DOC}]$ increases, $[\text{OH}\cdot]_{\text{ss}}$ also increases for all photosensitizer conditions studied. $[\text{OH}\cdot]_{\text{ss}}$ results were applied to the photochemical degradation of ibuprofen using literature-derived and empirically-determined rate constants. Hydroxyl radical accounts for nearly all of the indirect photochemical degradation of ibuprofen in OWC fulvic acid. In summary, photosensitizer levels in OWC influence $[\text{OH}\cdot]_{\text{ss}}$; for organic compounds that can be degraded by hydroxyl radical, the rate of degradation will depend heavily on the photosensitizing conditions of the wetland.

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