PHOTOLYSIS OF METOLACHLOR AND TRICLOCARBAN SENSITIZED BY NATURAL WATER CONSTITUENTS

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By

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ABSTRACT

Anthropogenic activity introduces a variety of synthetic organic compounds (SOCs) to surface waters. Among these are herbicides, pesticides, fertilizers, pharmaceuticals, and personal care products. Wetlands are known to be well suited to photolysis due to shallow depths and large surface area. In addition, they have been shown to contain species such as dissolved organic matter (DOM) and total nitrates (nitrate and nitrite) that can enhance the degradation of SOCs through indirect, or sensitized, photolysis. The major goal of this research is to determine to what extent these wetland constituents can increase the rate of degradation of an herbicide: metolachlor and an anti-bacterial compound: triclocarban. In particular, the significance of DOM origin on its reactivity was examined. For metolachlor, the influence of concentration on reactivity was also explored.

In order to probe the significance of DOM origin, fulvic acid isolates were chosen to represent a spectrum of chemical composition. Pony Lake, Antarctica fulvic acid (PLFA) was chosen to represent microbially derived, aliphatic organic matter while Suwannee River fulvic acid (SRFA) from Fargo, Georgia, was chosen to represent terrestrially derived, aromatic organic matter. Fulvic acid isolated from Old Woman Creek near Huron, Ohio, (OWCFA) was chosen to represent the median between the microbial and terrestrial end-members. For 65 µM metolachlor, the source of DOM was not found to significantly influence reactivity. However, at 0.5 μ M metolachlor, SRFA reacted significantly faster than either OWCFA or PLFA indicating terrestrially derived DOM is more reactive towards metolachlor. For 0.5 μ M triclocarban, PLFA reacted significantly faster than OWCFA or SRFA. This indicates that DOM reactivity towards contaminants varies not only with DOM origin, but also with the contaminant being examined.

To determine the degradation pathway for the two compounds examined, scavenging and sub-oxic experiments were performed. For metolachlor, isopropanol was used to quench hydroxyl radical (•OH) in the reaction solution. At 65 μ M metolachlor, the reaction was quenched 20-30%, while at 0.5 μ M metolachlor the reaction was quenched by 50-60%. Also for 65 μ M metolachlor, the influence of the addition of nitrate on reactivity was examined and found to be much more significant than DOM at concentrations of nitrate above 0.2 mM. For triclocarban, methanol was used for quenching •OH. At 0.5 μ M triclocarban, methanol quenched the reaction by 20-30% depending on the fulvic acid being used.

For both chemicals, argon sparging of the working solutions was performed for 90 minutes to determine the importance of triplet DOM (³DOM). In the case of metolachlor, argon sparging did not significantly affect the rate of degradation indicating that neither ³DOM nor reactive oxygen species (ROS) such as singlet oxygen ($^{1}O_{2}$), peroxyl radical (ROO•), and superoxide (O_{2}^{-}) are primary transients leading to degradation. However, for triclocarban, argon sparging increased the rate of reaction from 26-56% indicating that ³DOM does play a significant role in degradation. It also indicates that the extent to

which ³DOM influences reactivity varies considerably with the fulvic acid being examined. Thus, wetland constituents significantly enhance the degradation rate of SOCs.

DEDICATION

Dedicated to Jacques,

for his love, patience, and faith

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PUBLICATIONS

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TABLE OF CONTENTS

ABSTRACTii
DEDICATIONv
ACKNOWLEDGMENTS vi
VITAvii
PUBLICATIONS vii
LIST OF TABLES x
LIST OF FIGURES xi
CHAPTERS:
1. INTRODUCTION 1
1.1 Photochemistry in Natural Waters
1.2 DOM Photochemistry5
1.3 Nitrate Photochemistry7
1.4 Iron Photochemistry9
1.5 Reactive Oxygen Species (ROS) 11
1.6 Metolachlor and Triclocarban 12
1.7 Research Goals 14
2. PHOTOCHEMICAL TRANSFORMATION OF METOLACHLOR
2.1 Introduction 15
2.2 Materials and Methods 18

2.2.1 Chemicals and Reagents	
2.2.2 Natural Organic Matter Isolates and Wetland Water	19
2.2.3 Photolytic Reactions	20
2.2 Posults and Discussion	22
2.2.1 Direct and DOM Sensitized Photolyric	23 רכ
2.2.2 Identification of Detential Descrive Transients	25 20
2.2.2 The Dele of Nitrote	
2.3.3 The Role of Nitrate	
2.3.3 Photo-Fenton Pathway	
2.3.4 Low Concentration Study	
2.4 Conclusions	38
3. PHOTOCHEMICAL TRANSFORMATION OF TRICLOCARBAN	40
2.1 Introduction	40
2.1.1 Environmental Eate of Triclocarban	4 0 //1
3.2 Materials and Methods	43
3.2.1 Chemicals and Reagents	43
3.2.2 Dissolved Organic Matter Isolates and Wetland Water	
3.2.3 Photolytic Reactions	44
3.3 Results and Discussion	
3.3.1 Reaction Kinetics	
3.3.4 Argon Sparged Reactions	
3.3.5 Methanol quenching	
3.3.6 Photo-fenton Reaction	
3.4 Conclusions	57
4. CONCLUSIONS	59
4.1 Summary of Results	59
4.2 Environmental Significance	61
4.3 Future Work	61
UV-VIS SPECTRA	64
RIRLIOCRAPHY	67

LIST OF TABLES

Table 2.1 Pseudo-First-Order Rate Coefficients for 65 μ M Metolachlor ± 1 SD....... 27**Table 2.2** Pseudo-First-Order Rate Coefficients for 0.5 μ M Metolachlor ± 1 SD....... 37**Table 3.1** Pseudo-First-Order Rate Coefficients for Photolysis of Triclocarban ± 1 SD.48

LIST OF FIGURES

Figure 1.1 Photo-excitation scheme of dissolved organic matter (DOM)
Figure 1.2 Scheme showing the photolysis of nitrate and the production of radicals including •OH
Figure 1.3 Scheme showing the reaction mechanism of the photo-Fenton process 10
Figure 1.4 Scheme showing the reaction mechanisms for the formation of H_2O_2 in surface waters from the oxidation of Fe(II)
Figure 2.1 Proposed reaction scheme showing the base-catalyzed degradation of metolachlor where $R = -CH(CH_3)CH_2OCH_3$, $R' = -CH_2CH_3$, and $R'' = -CH_3$ (Wilson and Maybury, 2000)
Figure 2.2 UV-vis absorption spectrum of metolachlor normalized to $\lambda = 218$ nm 24
Figure 2.3 Metolachlor observed pseudo first order photo-degradation rate constants, k _{obs} , for direct photolysis (in deionized water) and photolysis sensitized by fulvic acids. These rate constants are corrected for light screening and are reported at the 95% confidence interval
Figure 2.4 The effect of isopropanol quenching on photo-degradation of metolachlor is shown by the solid triangles. The argon purged sub-oxic OWC FA experiment is shown by open circles and the air saturated experiment is shown by solid squares. These kinetics are not corrected for light screening
Figure 2.5 Metolachlor observed pseudo first order photo-degradation rate constants, k_{obs} , for direct photolysis (in deionized water) and photolysis in the presence of nitrate at various levels ranging from 0mM (Direct) to 1.0 mM with grey striped bars representing experiments conducted with Old Woman Creek Fulvic Acid (OWC FA), white striped bars representing experiments conducted in deionized water, and the white bar representing photolysis in deionized water without nitrate. These rate constants are corrected for light screening and are reported at the 95% confidence interval

Figure 3.4 Degradation rate constants (k_{obs}) for direct photolysis (in deionized water) and sub-oxic (argong sparged) DOM experiments. These rate constants are reported at the 95% confidence interval.	53
Figure 3.5 Degradation kinetics of triclocarban showing the influence of the addition of 25 mM methanol to a PLFA solution.	of 55
Figure 3.6 Degradation rate constants (k_{obs}) for direct photolysis (in deionized water) and methanol quenched DOM reactions with triclocarban. These rate constants are reported at the 95% confidence interval.	56
Figure 3.7 Degradation rate constants (k_{obs}) for triclocarban direct photolysis and for fulvic acid solutions spiked with 20 μ M of FeCl ₃	57

CHAPTER 1

INTRODUCTION

The global human population is increasing exponentially and with such growth comes an ever rising demand for fresh water. For this reason, it is essential to maintain the quality and purity of surface and ground water resources for future generations. Unfortunately, anthropogenic activity threatens water quality in a variety of ways. Many of the goods and services that are enjoyed as part of modern life are dependent on industrial chemicals and pharmaceuticals. The sheer number of chemicals used industrially and in consumer products has risen considerably over the last century and especially in recent decades – some 8,300 chemicals are manufactured and sold in significant quantities in the United States annually (Hogue, 2007). Many of these enter the natural environment and may disperse and persist far beyond their useful lifetime (Kolpin et al., 2002).

Herbicides and pesticides are intentionally applied in controlled amounts, but may have unanticipated effects in surface waters due to runoff. Products used in the home including cleaning chemicals, pharmaceuticals, personal care products, and biogenic hormones (such as birth control or hormone replacement therapy) can enter surface waters after passing through wastewater treatment plants (WWTP) or septic systems as neither of these methods of water treatment effectively removes such chemicals from the finished effluent (Kolpin et al., 2002). Urban runoff that is not subject to wastewater treatment can also negatively impact surface water as it contains a variety of oils, road salts, trace metals, and chemicals from automobiles. These are just some of the ways in which human activity can negatively impact watershed integrity.

For many synthetic organic contaminants (SOCs), the environmental occurrence, transport, and ultimate fate are largely unknown (Kolpin et al., 2002). This is in part due to the analytical difficulty in assaying a complex mixture of very low concentrations and in part due to the sheer number of chemicals to be examined. Yet, the low concentrations do not negate the significance of the threat to water quality. SOCs can induce abnormal physiological processes and impair reproduction, increase cancer risks, and contribute to the formation of antibiotic-resistant strains of bacteria (Kolpin et al., 2002). There is also increasing concern over mixture toxicity – the possibility that chemicals may act either synergistically or antagonistically to increase or decrease total toxicity.

U.S. EPA regulations govern the majority of point sources such that most current pollution of surface water quality arises from non-point sources. Among these non-point sources is agricultural pollution – a mixture of fertilizers, silt, and various biocides. Surface waters are especially threatened in the spring when high concentrations of chemicals are applied and little to no vegetation exists to intercept overland flow from fields into streams. These constituents impact water quality not only directly but also in the way in which they impact the ecological cycles of surface waters. For example, excess nutrient loads in the Great Lakes region have led to increases in blooms of strains

of algae that produce toxins (Wilhelm et al., 2003).

Wetlands provide a buffer region between the site of introduction of chemical constituents to surface waters and larger water bodies. There are many aspects of wetlands that contribute to their ability to breakdown or sequester contaminants. Vegetation slows down water flow increasing the time for reaction to take place while. Sediments provide sorption sites and habitat for anaerobic microbial processes. Photolytic degradation is the primary abiotic degradation pathway for many anthropogenic constituents, and the physical characteristics of high surface area and shallow depth make wetlands well suited to photochemical reactions. Thus, an understanding of the factors that contribute to the degradation of contaminants in wetlands is critical to developing an accurate model for environmental fate of a given contaminant.

1.1 Photochemistry in Natural Waters

In natural waters, photochemical reactivity is limited to the upper most portion of the water column known as the photic zone. The depth of this photic zone varies considerably with water characteristics. Water with a high algal content or sediment loading will have a very shallow photic zone due to light absorption and scattering. In addition, dissolved organic matter (DOM) can absorb, or attenuate, sunlight which also decreases the depth of light penetration. A sub component of DOM, colored dissolved organic matter (CDOM) is the main UV absorbing species in surface waters and determines the depth of UV light penetration (Zepp, 2007; Markager and Vincent, 2000). Within the photic zone, there are two main categories of light initiated reactivity. There is direct photolysis in which contaminant A absorbs a photon of light, is excited to its singlet state ¹A, and undergoes chemical transformation to generate a different product species. This direct process is governed primarily by the chemical nature of the contaminant species itself. The presence of substructures, known as chromophores, determines the ability of a molecule to absorb light. Important chromophores include functional groups such as alkenes, carbonyls, aromatic and heterocycles, and nitro groups. The simplest way to determine a molecule's ability to absorb light is to measure its UV-vis absorption spectrum. The wavelengths at which the compound has a high extinction coefficient are those where absorption is likely. Direct photolysis in natural light is only possible if the contaminant of interest absorbs light in the UV-visible range (280-750 nm).

In the presence of O_2 , it is also possible for intersystem crossing to occur from ¹A to ³A, the triplet excited state of contaminant A. This is important because triplet states are more stable and therefore more able to react with other excited state species. Such reaction of contaminant molecules is one form of indirect photolysis. Other indirect pathways include reactive transients acting on the ground state of the contaminant without excitation of the contaminant. Natural waters contain a variety of constituents that are capable of producing reactive intermediates. Among these are dissolved organic matter (DOM), nitrate (NO₃⁻) and nitrite (NO₂⁻), and trace metals.

1.2 DOM Photochemistry

The photochemical role of DOM must be considered when examining the environmental fate of any surface water contaminant as it is ubiquitous and is a source for many reactive transients. It is possible for DOM to sensitize several indirect photolytic pathways and the pathways will vary both with the contaminant of interest and origin of the DOM (Chin et al., 2004). Conversely, chromophores present within DOM can act as filters to photons of certain wavelengths (attenuation) or DOM can scavenge reactive transients, further complicating its role in photolytic degradation (Torrents et al., 1997; Walse et al., 2004).

Many of the excited state reactions of DOM are not well understood. The formation of reactive transients can be observed through the use of probe compounds, but it is difficult to determine if these transients arise from singlet DOM (¹DOM) or triplet DOM (³DOM). In any case, it is known that DOM can react with other species in natural waters such as O₂ to form reactive transients including singlet oxygen (¹O₂), hydroxyl radical (•OH), hydrogen peroxide (H₂O₂), hydroperoxyl radical (HO₂•), superoxide (O₂•), and organic peroxyl radicals (ROO•) (Cooper et al., 1989; Miller, 1994). DOM can also release energy by ejecting electrons producing solvated electrons (e⁻_{aq}) or undergo photoionization to form free radicals (Sandvik et al., 2000). One of the ROS mechanisms that is fairly well known is the formation of singlet oxygen – ground state oxygen (³O₂) undergoes energy transfer with ³DOM (Faust and Hoigne, 1987) to form the

reactive species, ¹O₂. These reactive oxygen species can then act on the contaminant of interest leading to increases in degradation rates. In addition, if the energies match appropriately, ³DOM can react with a contaminant of interest directly through energy or electron transfer (Canonica et al., 2001).



Figure 1.1 Photo-excitation scheme of dissolved organic matter (DOM).

Alternatively, ³DOM can react with a contaminant of interest via electron transfer or hydrogen atom abstraction. It can also be quenched by O_2 (the most common quencher) in aerobic systems or by other DOM molecules and solutes in anoxic systems (Bruccoleri et al., 1993; Gorman and Rodgers, 1986). Which species are formed in a given system is determined by the chemistry of the natural water and the composition of the DOM. The chemical nature of DOM can vary considerably -- from primarily autochthonous materials that are derived within an aquatic system to allochthonous materials derived from higher plants as well as animal and soil materials (Brown et al., 2004; Fimmen et al., 2007). Autochthonous materials are derived from algal or microbial products and are typified by aliphatic character while allochthonous materials are derived from lignins and polysaccharides and are characterized by high levels of aromaticity. Additionally, such differences in structure can lead to significant variability in DOM reactivity towards organic contaminants. Thus, it is important to consider the origin of the DOM to accurately assess reactivity towards SOCs.

1.3 Nitrate Photochemistry

The photochemical reactivity of nitrate in surface waters was discovered in the early 1970s (Brezonik and Fulkerson-Brekken, 1998). Since then, the potential for nitrate to act as a photosensitizer for the breakdown of environmental pollutants has been well documented (Sharpless, et al., 2003; Miller and Chin, 2005). Under irradiation at wavelengths greater than 290 nm, nitrate can produce highly reactive hydroxyl radicals (•OH) with quantum yields in the range of 9.2-17 x 10^{-3} M (Maybury and Crosby, 1996). Nitrite is a photoproduct of nitrate which can itself produce hydroxyl radical when irradiated between 298 and 371 nm (Miller and Chin, 2002). In an agricultural watershed, the concentration of nitrate can be sufficient to produce high steady-state concentrations of •OH (Miller and Chin, 2002). Though the concentration of nitrate can be on the order of 1mM in an agricultural watershed in spring, this varies considerably throughout the year making the contribution of nitrate to contaminant degradation seasonally dependent (Miller and Chin, 2005). By spiking water samples of contaminants with NaNO₃ and observing the subsequent enhancement of photolysis rates,

it is possible to correlate reactivity to nitrate generated •OH (Dimou et al., 2004; Miller and Chin, 2002; Torrents et al., 1997).

As can be seen in Figure 1.2, there are two primary photochemical pathways induced by irradiation of nitrate. Upon absorption of a photon, excited state nitrate can decay to nitrite (NO_2^-) and atomic oxygen $(O(^3P))$ or to nitrogen dioxide (NO_2) and an oxygen radical $^{\circ}O^-$. The atomic oxygen most often reacts with dioxygen to produce ozone (O_3) , which subsequently either reacts with NO_2^- or decomposes to hydroxyl radical, $^{\circ}OH$ (Zepp et al., 1987). Importantly, the oxygen radical reacts with water to form additional hydroxyl radical.



Figure 1.2 Scheme showing the photolysis of nitrate and the production of radicals including •OH.

Nitrite ions strongly scavenge hydroxyl radical and the effect is more prominent with higher initial concentrations of nitrate as more nitrite is produced (Zepp et al., 1987). As stated above, hydroxyl radical can also be scavenged by DOM. Thus, the potential reactivity of the nitrate produced hydroxyl radical depends on the overall composition of the water.

1.4 Iron Photochemistry

Iron is one of the most common metals in surface waters and so its reactions are significant to the environmental fate of contaminants. Naturally occuring iron plays an important part in many redox cycles including acid mine drainage, mineral solubility, and catalysis of natural water processes. Indeed, iron has been used in engineered systems to photocatalyze the degradation of herbicides and pesticides (King, 1998). Iron reacts through both primary and secondary photolytic processes. The primary processes include photolysis of iron hydroxyl complexes while the secondary processes include the photo-Fenton pathway. (Faust and Hoigné, 1993; Voelker et al., 1997). Here we will focus on the secondary reaction processes as Fenton's reagent has been shown to be highly effective at degrading SOCs (Sedlak and Andren, 1991). The two main components of the photo-Fenton pathway are shown in Figure 1.3.



Fe(III) + OH + OH

Figure 1.3 Scheme showing the reaction mechanism of the photo-Fenton process.

The first step is reduction of Fe(III) to Fe(II), which is followed by reaction of Fe(II) with hydrogen peroxide (H₂O₂) to form hydroxide (OH) and hydroxyl radical (•OH) and regenerate Fe(III) (White et al., 2003; Zepp et al., 1992). Reduction to Fe(II) can be achieved in a number of ways including photolysis of organic or inorganic complexes, reduction by superoxide, reduction at cell surfaces, or abiotic reduction by humic acids (Emmenegger et al., 1998; Emmenegger et al., 2001). The kinetics of the photo-Fenton pathway are sensitive to pH, salinity, temperature, and the presence of organic ligands. Under aerobic conditions at neutral pH, the dominant form of iron in natural waters is Fe(III), which has very low solubility. Also, photochemical reactions in natural waters can rapidly generate Fe(II) from Fe(III)-organo complexes via ligand to metal charge transfer (LMCT) reactions. These ligands can increase Fe(III) solubility and the absorption of photons (Southworth and Voelker, 2003). In addition, humic substances can reduce Fe(III) to Fe(II) in the absence of light. (Voelker and Sulzberger

1996; Voelker et al., 1997).

In surface waters, the H_2O_2 required for the photo-Fenton reaction can be formed in a number of ways as shown in Figure 1.4. Oxidation of Fe(II) can generate superoxide radical (O_2^{\bullet}), which can further react with Fe(II) to form H_2O_2 . In addition, dismutation of hydroperoxyl / superoxide radicals can form H_2O_2 either alone or catalyzed by Fe(II). DOM can also participate in this part of the photo-Fenton reaction by sensitizing the formation of H_2O_2 (Fukushima and Tatsumi, 2001).

 $Fe (II) + O_2 \longrightarrow Fe (III) + O_2^{-}$ $Fe (II) + O_2^{-} \longrightarrow Fe (III) + H_2O_2$ $2HO_2^{-} + O_2^{-} + H^+ \longrightarrow H_2O_2 + O_2$

Fe (II) + 2HO₂· O₂· + H⁺ \longrightarrow Fe (III) + H₂O₂

Figure 1.4 Scheme showing the reaction mechanisms for the formation of H_2O_2 in surface waters from the oxidation of Fe(II).

1.5 Reactive Oxygen Species (ROS)

Reactive oxygen species (ROS) including singlet oxygen (${}^{1}O_{2}$), hydroxyl radicals (•OH), hydrogen peroxide (H₂O₂), hydroperoxyl radical (HO₂•), superoxide (O₂•⁻), and organic peroxyl radicals (ROO•) are nearly ubiquitous in surface waters (Blough and Zepp, 1995). The production of these ROS as well as their precursors and products is primarily due to abiotic photochemical reactions of chromophores naturally present in surface waters. Colored dissolved organic matter (CDOM) is the primary source for

these sensitizing chromophores; however, DOM can also be a sink or quencher of these transient species (Lindsey and Tarr, 2000). Thus, the steady-state concentration for many ROS is very low in natural waters (Faust and Hoigne, 1987). ROS are environmentally relevant as they often degrade high molecular weight constituents into smaller, more readily metabolized, organic compounds, thereby purifying the water column.

Superoxide (O_2^{-}) is a poor nucleophile and acts principally as a one-electron reductant or as an oxidant. Singlet oxygen is thought to be formed through energy transfer from the triplet excited state of colored dissolved organic matter (³CDOM*) to ground state (triplet) dioxygen (³O₂). Hydroxyl radical production can occur either through the photo-Fenton pathway described above or by direct photolysis of DOM itself (Grannas et al., 2006). As its absorption spectrum does not significantly overlap with the solar spectrum, photolysis of H₂O₂ does not generally lead to the formation of •OH (Blough and Zepp, 1995). Peroxyl radicals (ROO•) can be formed from CDOM by a number of processes including H-atom abstraction, electron transfer, or homolytic bond cleavage (Blough and Zepp, 1995). Of the ROS that have been identified and studied, hydroxyl radical is the most reactive and least selective towards both organic and inorganic species, making it an important transient in the degradation of SOCs (Lam et al., 2003). Thus, hydroxyl radical initiated degradation will be the most important radical pathway in shallow water bodies, such as wetlands (Armbrust, 2000).

1.6 Metolachlor and Triclocarban

The two surface water contaminants examined in this study, metolachlor and

triclocarban, were chosen for their widespread use, environmental persistence, and potential for toxicity. Metolachlor is a pre-emergent herbicide used primarily on corn, soybeans, and sorghum with total annual use of approximately 67 million pounds (Kolpin, 1998). It is considered slightly toxic and potentially carcinogenic (Hill et al., 1997). It currently has no EPA Maximum Contaminant Level (MCL), but does have a Health Advisory Level of 100 ppb. Metolachlor can be considered somewhat recalcitrant with a measured half-life of 74 hours (Wilson and Maybury, 2000).

Triclocarban is an antimicrobial compound that, in addition to threatening drinking water, may contribute to the development of antibiotic resistant bacteria. Though it has been widely used in household products since 1957, the environmental fate of triclocarban has remained largely unexamined. It is both toxic and persistent and recent research found triclocarban in 60% of 85 streams tested (Halden and Paull, 2005). This is not surprising considering 500,000 – 1,000,000 lb of triclocarban are used in the United States each year in cosmetics and personal care products (Halden and Paull, 2005).

1.7 Research Goals

Photo-induced degradation of surface water contaminants is dependent on a multitude of factors. Among these are contaminant concentration, presence and character of DOM, nitrate concentration, trace metals and their complexes, nitrate concentration, and the chemical nature of the contaminant.

Specific objectives of this research include:

- elucidating and evaluating the role of direct and indirect photolysis in the degradation of metolachlor (Chapter 2) and triclocarban (Chapter 3) in polychromatic light representative of the solar spectrum. These two chemicals were chosen as they are widely used in the United States and have been detected as surface water contaminants.
- conducting photodegradation experiments in the presence of DOM isolated from our wetland field sites (Old Woman Creek) and isolates from the International Humic Substance Society (IHSS). These IHSS standards (Pony Lake and Suwannee River fulvic acids) have been well characterized in previous literature and so allow for straightforward comparison to other photolytic studies.
- examing the ability of wetland water constituents to promote target contaminant (metolachlor and triclocarban) degradation. Through the use of •OH scavenging isopropanol and by altering reaction conditions, transients responsible for reactivity were identified (Chapter 2 and 3).

CHAPTER 2 PHOTOCHEMICAL TRANSFORMATION OF METOLACHLOR

2.1 Introduction

Surface waters in the U.S. are a source for both drinking water and recreation, thus the fate of contaminants introduced to surface waters is of concern. Metolachlor was chosen as a contaminant of interest due to its widespread agricultural use in the United States as well as its presence in our field site. The environmental fate of pesticides in surface waters is an important aspect of total water quality as they contribute significantly to non-point source pollution. Of the compounds currently used on crops in the U.S., several are known or suspected carcinogens and/or endocrine disruptors (U.S. EPA, 2005). In addition, agricultural run-off contains high levels of nitrates which can lead to eutrophication and high nitrate levels in drinking water. For these reasons, agricultural non-point source pollution is recognized as a primary source of water quality impairment for lakes, rivers, wetlands, estuaries, and ground water (U.S. EPA, 2000).

Metolachlor is second only to glyphosate as the most commonly used herbicide in the United States. Thus, it has frequently been detected in both groundwater and surface waters (Kolpin, 1998; Wu et al., 2007). It is primarily a non-point source pollutant found in surface waters following runoff events after application to farmlands (Richards and Baker, 1993; Southwick et al., 2003). Metolachlor is a pre-emergent herbicide used primarily on corn, soybeans, and sorghum with total annual use of approximately 67 million pounds (Kolpin, 1998). It is considered slightly toxic and potentially carcinogenic. It currently has no EPA Maximum Contaminant Level (MCL), but does have a Health Advisory Level of 100 ppb (0.35 μ M). Wilson and Maybury (2000) have found that metolachlor is degraded photochemically with a measured half-life of 74 hours under continuos irradiation in a solar simulator. In addition, they proposed a base catalyzed mechanism as shown in Figure 2.1. It is possible that a similar mechanism could proceed via the production of •OH by sensitizing species within the water column.



Figure 2.1 Proposed reaction scheme showing the base-catalyzed degradation of metolachlor where $R = -CH(CH_3)CH_2OCH_3$, $R' = -CH_2CH_3$, and $R'' = -CH_3$ (Wilson and Maybury, 2000).

Wetlands have an abundant supply of potential photosensitizers, such as dissolved organic matter (DOM) and nitrate and are well suited to indirect photo-degradation of contaminants. DOM is especially advantageous in that it is ubiquitous to surface waters and is capable of leading to a multitude of reactive oxygen species (ROS) and other non-ROS transients such as triplet DOM (³DOM). In addition, the chromophores present in the DOM vary depending on its source. Thus, DOM can potentially sensitize several indirect photolytic pathways and the pathways will vary both with the contaminant of interest and origin of the DOM (Chin et al., 2004). It is also possible for chromophores present within DOM to act as filters to photons of certain wavelengths or scavenge reactive transients, further complicating the role of DOM in photolytic degradation (Torrents et al., 1997).

Another chemical constituent found in agricultural watersheds that contributes significantly to photochemistry is nitrate. When exposed to sunlight, nitrate forms significant quantities of •OH (Zepp et al., 1987). In waters receiving agricultural runoff, nitrate concentrations can vary seasonally from 0.1mM up to 1.0 mM (Miller and Chin, 2002; Miller and Chin 2005). At such nitrate concentrations, the •OH formed becomes an important ROS for contaminant degradation (Zepp et al., 1987). Indeed, it is possible for nitrate to become a more important photosensitizer than DOM in natural waters receiving agricultural runoff (Wilson and Maybury, 2000; Torrents et al., 1997).

Phototransformation kinetics are complex and depend not only on the constituents present, but in some cases the concentration of each constituent (Miller and Chin, 2005). In this research, we assess the photoreactivity of metolachlor in the presence of DOM and

nitrate in wetland water collected from an agricultural watershed in order to determine the dominant sensitization pathway. We also examined the influence of DOM origin on reactivity. Fulvic acid, or the acid soluble fraction of DOM, accounts for 50% of total DOM in fresh water systems (Brown et al., 2004). Thus, we performed photolysis experiments using fulvic acid isolates representing the spectrum of possible DOM origins - from an autochthonous end member composed of microbial and algal derivatives to an allochthonous end member composed of terrestrial plant derivatives. For this study, the autochthonous endmember came from Pony Lake, Antarctica which is completely free of inputs from higher plants. The allochthonous endmember is from the Suwannee River in GA, USA, an acidic blackwater swamp. An additional sample representing a mixture of autochthonous and allochthonous material is represented by Old Woman Creek, an estuary feeding into Lake Erie in Huron, OH. It was our intention to investigate to what extent these chemical differences would impact the degradation kinetics of metolachlor. These experiments were conducted at two significantly different concentrations of metolachlor: 65 μ M and 0.5 μ M. The latter is more representative of environmental concentrations due to agricultural runoff.

2.2 Materials and Methods

2.2.1 Chemicals and Reagents

Materials. All chemicals and reagents were purchased commercially and used without further purification. Chemicals and reagents were acquired from the following: Metolachlor (99.5%) from Chem Services West Chester, PA; isopropanol (Optima),

acetonitrile (Optima), sodium hydroxide (NaOH; analytical reagent) from Mallinckrodt; potassium hydrogen phthalate (KHP), sodium nitrate, *p*-nitroanisole, and pyridine from Aldrich (Milwaukee, WI); AG-50W-X8 resin from Bio-Rad (Hercules, CA); argon (4.8 grade) from Praxair. The reference fulvic acids Suwannee River Fulvic Acid (SRFA) Lot #1R101F-1 and Pony Lake Fulvic Acid Lot #1R109F were purchased from the International Humic Substance Society (IHSS). All glassware was washed with NOCHROMIX Cleaning Reagent (Godax Laboratories, Inc) in concentrated sulfuric acid and all plastics were washed with 10% HCl prior to use.

2.2.2 Natural Organic Matter Isolates and Wetland Water

Natural organic matter XAD-8 isolates were chosen to represent a spectrum of reactivity. *Suwannee River Fulvic Acid (SRFA)* This is an International Humic Substance Society (IHSS) fulvic acid standard. The source of Suwannee River is located in the Okefenokee Swamp and contains organic matter derived from sphagnum moss and cypress tree litter. Thus, the organic matter is rich in materials external to the water column. The water exhibits a low pH and so there is minimal primary productivity within the water column. These qualities serve to make the fulvic acid an allochthonous, or terrestrial endmember on the fulvic acid spectrum.

Pony Lake Fulvic Acid (PLFA) This is an International Humic Substance Society (IHSS) fulvic acid standard. The source, Pony Lake, is located in Antarctica and receives no terrestrial inputs as there are no higher land plants on the continent. Thus, it is rich in algal and microbial organic matter constituents derived within the water column and so is

an autochthonous fulvic acid endmember.

OWC Fulvic Acid (OWC FA) This was isolated in our lab according to standard protocols. Old Woman Creek (OWC) is a temperate eutrophic wetland located on the south shore of Lake Erie. It is a natural wetland and, due to its location, it receives significant agricultural runoff from a watershed of approximately 69 km² in size. This wetland receives a significant amount of suspended solids, fertilizers, and pesticides. We isolated the fulvic acid fraction of OWC DOM by adsorption to non-ionic XAD-8 resin under acidic (pH 2) conditions, elution under alkaline conditions (pH 10), and deionization with Amberlite AG-50 cation exchange resin (H+-saturated) according to established protocols (Leenheer, 1981; Thurman and Malcolm, 1981). The solution was then freeze-dried and stored at room temperature until use.

2.2.3 Photolytic Reactions

Prior to photolysis, a stock solution of metolachlor was prepared in acetonitrile. From this stock solution, photolysis solutions were prepared by evaporating an aliquot of stock and reconstitution in the appropriate matrix. (NaNO₃ and/or fulvic acid). Final concentrations were 0.5 or 65μ M metolachlor, 0 – 1.0 mM NaNO₃, and 4 - 6 mg C/L DOC. To probe the role of hydroxyl radical, photolysis experiments with excess isopropanol (25mM) as an •OH scavenger were performed. Suboxic experiments were purged with argon for 90 minutes and transferred to quartz tubes in a glove box under a 95% N₂/ 5% H₂ atmosphere.

In all cases, solutions were irradiated in air-tight quartz tubes sealed with Teflon caps

with no headspace. Photolysis experiments were performed in a CPS+ Solar Simulator (Atlas Electric Devices) with an 1100 watt xenon arc lamp. By using an H filter, the "Solar standard" filter, the output of the simulator is made to mimic the spectrum of natural sunlight for wavelengths from 290 to 800 nm. The lamp was set to 500 W/m^2 and the radiometer readings were approximately 2.9 mW/cm² for all photolysis experiments. Initial pH was adjusted to 8.1 and was constant over the course of the reaction. Dark controls were run concurrently for each photolysis experiment, but did not result in degradation under any conditions examined. Temperature was measured using a black standard temperature (BST) probe set to 30°C. Irradiation experiments were carried out for 48 hours, with samples sacrificed every six hours for High Pressure Liquid Chromatography (HPLC) analysis to determine loss of the parent compound. A direct aqueous injection (200µL) was made from each vial into the HPLC and separation was achieved using a Novapak Waters C-18 reverse-phase chromatography column and detected using a Waters 2487 dual λ Absorbance detector at 212nm for 0.5µM and 254nm for 65µM. Mobile phase for the analysis was 60% acetonitrile / 40% Milli-Q (v/v) and the flow rate was 1.0 mL/min. Kinetic data were fit to a pseudo-first order equation using Microsoft Excel and SigmaPlot 10.0. Rate coefficients for metolachlor degradation were determined using a least-squares fit of the observed data to a pseudofirst order kinetics model with $R^2 \ge 0.97$ for all reactions.

2.2.3.1 Actinometry Corrections

In order to monitor photon flux and to check for changes in the light intensity of the lamp, chemical actinometry was conducted periodically using the *p*-nitroanisole

(PNA)/pyridine (PYR) system (Dulin and Mill, 1982). Over the course of this research, no significant changes in light intensity were observed. The following equation is used to compare reaction rates between the solar simulator and natural sunlight using PNA's equivalent rate constant (k) at solar noon in June at 40° N:

$$\mathbf{k} = \phi_{\lambda} \sum \varepsilon_{\lambda} \Lambda_{\lambda} \tag{1}$$

where ϕ is PNA's quantum yield, ε is the molar absorption coefficient of PNA, and A is sunlight irradiance for a specific wavelength (Leifer, 1988). We calculated a natural sunlight rate constant of 2.83 d⁻¹ over a range of 290 to 800 nm and a rate constant of 10.51 d⁻¹ in our solar simulator or 3.7 times faster in the simulator. Thus, the metolachlor degradation rates presented here are significantly faster than would be observed in natural sunlight due to the intensity of the light source used. Other factors including surface scattering of incident light and attenuation within the water column would further slow kinetics in a natural setting as compared to the presented results. However, these phenomena would presumably only serve to slow the kinetics, not alter the relevant degradation pathways.

2.3 Results and Discussion

2.3.1 Direct and DOM Sensitized Photolysis

Direct photolysis of metolachlor has been observed previously and has been shown to be pH independent (Wilson and Maybury, 2000). Direct photolysis can be predicted based on the absorption spectrum of metolachlor shown in Figure 2.2. The functional groups of metolachlor exhibit some absorbance above 290 nm. However, the absorption is weak and one would anticipate direct photolysis to be slow, which is indeed the case. Direct photolysis of metolachlor was investigated using 65 μ M and 0.5 μ M working solutions of Metolachlor in MilliQ water pH adjusted to 8.1 and the results for 65 µM photolysis are shown with fulvic acid photolysis experiments in Figure 2.3. For 65 µM metolachlor, we observed a half-life of 45 hrs, nearly twice as fast as that found by Wilson and Maybury (2000) at 18 M metolachlor. This considerable difference could be due to differences in the settings at which the systems were operated – our system was run at 500 W/m^2 with radiometer readings averaging 2.9 mW/cm². Dark controls were run concurrently with each photolysis experiment by wrapping samples in aluminum foil and placing them in the solar simulator with the rest of the photolysis tubes. However, under all conditions examined dark reactions were found to be insignificant.



Figure 2.2 UV-vis absorption spectrum of metolachlor normalized to $\lambda = 218$ nm.

Photolysis experiments sensitized by fulvic acid and OWC whole water are shown in Figure 2.2. The presence of any of the three fulvic acids tested as well as the whole water significantly increases the rate of degradation. The order of reactivity for sensitized photolysis is OWC FA < OWC WW < SRFA < PLFA. with the half-life for each rate coefficient given in Table 2.1. Assuming an 8 hour day under summer sun, these half-lives translate to 4.3 (for PLFA) – 5.7 (for direct) days of natural sunlight.


Figure 2.3 Metolachlor observed pseudo first order photo-degradation rate constants, k_{obs} , for direct photolysis (in deionized water) and photolysis sensitized by fulvic acids. These rate constants are corrected for light screening and are reported at the 95% confidence interval for individual experiments.

As discussed above, there is a significant difference in the chemical composition of the two end member fulvic acids. Microbially derived DOM, such as that from Pony Lake is more aliphatic in nature, whereas terrestrially derived DOM, such as that from Suwannee River is more aromatic in nature (Fimmen et al., 2007; McKnight et al., 2001). Given these structural differences, it was anticipated that photo-reactivity with metolachlor would vary significantly between SRFA and PLFA. However, there is minimal difference in reactivity at 65 μ M metolachlor as both SRFA and PLFA react approximately 30% faster than direct photolysis. In addition, both OWC fulvic acid and whole water react approximately 15% faster than direct photolysis indicating that there is minimal difference in reactivity between the whole water and the fulvic acid fraction. As the nitrate in the whole water is very low and the levels of dissolved organic carbon (DOC) are similar for both, the similarity in reactivity indicates that fulvic acid is a good proxy for whole water DOM. Also, the 15% difference in reactivity between the two end members and OWCFA is not large enough to be statistically significant. Thus, at 65 μ M metolachlor it seems that the degradation pathway is not primarily dependent upon the chemical composition of the DOM, even though the presence of DOM does enhance reactivity. It is interesting to note that both OWC fulvic acid and whole water react more slowly than SRFA and PLFA, though the differences are not statistically significant. However, at this time, I cannot offer an explanation for this observation.

In addition to sensitizing photolysis DOM can preferentially absorb photons, decreasing the photons available to initiate contaminant degradation creating an effect known as light screening. This process occurs through the action of chromophores, or light absorbing moieties within the DOM structure. In order to quantify such light screening in the whole water and fulvic acid solutions, we applied a correction factor that was calculated for each rate constant. Using a UV-Vis absorbance scan for each sample, a light screening factor is calculated for each wavelength according to the following equation:

$$S_{\lambda} = [1 - 10^{-(1.2)(A)}] / (2.3)(1.2)(A)$$
(2)

where A is absorbance, 1.2 is an average distribution function of light in natural waters, (Schwarzenbach et al., 2003; Zepp and Cline, 1977) and $S_{\lambda} = 1.0$ if no attenuation by DOM occurs. We plotted S_{λ} versus wavelength and integrated the area under the curve to

(1.0)(1)

determine the overall screening factor over the wavelengths of interest (290 to 375 nm), the region in which DOM has the highest absorption. The screening factors for the whole water and the fulvic acids are given in Table 2.1. The corrected rate constants are $(k_{corrected} = 0.0215)$ for SRFA, $(k_{corrected} = 0.0191)$ for OWC FA, $(k_{corrected} = 0.0218)$ for PLFA, and $(k_{corrected} = 0.0198)$ for the OWC whole water. As can be seen in Figure 2.3, these rate constants are not statistically different from one another. They are, however, significantly faster than direct photolysis.

DOM	[DOC] (mg/L)	k _{obs} (hr⁻¹)	Σ S₂₉₀₋₃₇₅	Fe _t	[NO₃ ⁻]	half-life (hr)
Direct		$(1.53 \pm 0.1) \times 10^{-2}$	not applicable			45.3
OWC WW	6.161	$(1.81 \pm 0.1) \times 10^{-2}$	0.92	0.021mM	0.071mM	38.3
SRFA	6.473	$(1.95 \pm 0.2) \times 10^{-2}$	0.91			35.5
OWCFA	6.335	$(1.75 \pm 0.1) \times 10^{-2}$	0.92			39.6
PLFA	6.646	$(2.01 \pm 0.1) \times 10^{-2}$	0.92			34.5

Table 2.1 Pseudo-First-Order Rate Coefficients for 65 μ M Metolachlor ± 95% confidence interval.

Our analysis indicates that at 65 μ M metolachlor, the origin of DOM does not significantly affect the rate of photodegradation as there was no statistically relevant difference observed among the three sources of DOM either with or without correction for light screening. Under these experimental conditions the source, and therefore variations in the chemical structure, of DOM does not appear to impact the photodegradation of metolachlor. In addition, the extent to which OWC whole water increases the rate of photolysis is statistically the same as for the OWC fulvic acid. This

supports the assumption that the fulvic acid fraction is the most photo-active portion of the DOM and therefore the most experimentally relevant.

2.3.2 Identification of Potential Reactive Transients

The increase in degradation that is observed upon addition of fulvic acid can be attributed to indirect photolysis. More specifically, triplet state DOM (³DOM) can react with ground state metolachlor through energy transfer or by excited-state DOM reacting with oxygen (O_2) to form reactive oxygen species (ROS) that, in turn, react with metolachlor. It is straight forward to design an experiment to eliminate potential transient species responsible for this degradation. Formation of any of the possible ROS except •OH requires the presence of oxygen while both ³DOM and hydrated electron $e_{(aq)}$ are quenched by the presence of oxygen. Thus, removal of oxygen by argon sparging would significantly alter the kobs if any of these pathways contributes significantly to metolachlor degradation. For a ROS driven pathway, removal of oxygen would remove the source of reactive radicals and k_{obs} would decrease. In the case of a ³DOM pathway, removal of oxygen would remove the primary quenching species and k_{obs} would increase. Similarly, if hydrated electron played a significant role in photolysis, removing oxygen would increase the rate of reaction by removing a competing scavenger (Cooper et al., 1989). In order to investigate these possibilities and minimize the concentration of dissolved oxygen to the greatest extent possible, working solutions of OWCFA and OWCWW were sparged with Argon for 1.5 hours before being sealed into quartz reaction tubes under an inert environment. The amount of dissolved oxygen removed

was not measured. It is not possible to eliminate all dissolved oxygen from the solution using this technique, but a great enough fraction of the dissolved oxygen is removed that if an effect exists it will be observed.

In both cases, argon sparging had virtually no impact on the rate of degradation of metolachlor. It can be because the two pathways are occurring simultaneously and simply balance each other giving the appearance that sub-oxic conditions do not alter the rate of metolachlor degradation. Another possibility is to assume that the ROS and ³DOM pathways are mutually exclusive. If the assumption is valid, the argon experiment indicates that ³DOM does not play a significant role in metolachlor degradation. In addition, since argon sparging did not diminish the rate of metolachlor degradation, it can be assumed that singlet oxygen ($^{1}O_{2}$), peroxyl radical (ROO•), and superoxide (O_{2}^{-}) are not significant reactive transients leading to degradation.

Since removal of oxygen did not decrease the rate of degradation, there must be a radical at work that does not require the presence of oxygen to form. The most common radical meeting this requirement is •OH, which is known to play an important role in the breakdown of many organic contaminants and can be derived from the photolysis of DOM. (Miller and Chin, 2005) It is possible to estimate the role of •OH in the degradation of metolachlor. We can express the rate of metolachlor photolysis as follows:

$$-d[Met]/dt = k_{obs}[Met] = k_{dir}[Met] + k_{\bullet OH} [Met][\bullet OH]_{ss}$$
(3)

where [Met] represents metolachlor concentration, k_{dir} is the first order rate constant for the direct photolytic pathway, and t represents time. Using the reported second order rate constant for metolachlor ($k_{\bullet OH}$) with $\bullet OH$, 9.1 x 10⁹ L/mol-s (Wu et al., 2007) we can estimate the pseudo first-order rate constant (k') for the reaction between $\bullet OH$ and metolachlor:

$$\mathbf{k}' = \mathbf{k}_{\bullet OH} \mathbf{x} \left[\bullet OH \right]_{ss} \tag{4}$$

where k_{•OH} is the second order rate constant and [•OH]_{ss} for OWC whole water was measured in our lab (using the method of Zhou and Mopper, 1990) and found to be $1.4 \times$ 10^{-16} mol/L (Houtz, 2007). The resulting calculated rate of reaction between •OH and metolachlor in OWC whole water $(4.6 \times 10^{-3} \text{ hr}^{-1})$ is one quarter of the photolysis rate constant ($k_{obs} = 0.0181 \text{ hr}^{-1}$). This indicates that the presence of •OH forming sensitizers makes a significant contribution to the degradation of metolachlor. In addition, an experiment run with OWC whole water and an •OH scavenger, 25mM isopropanol, decreased the rate of degradation by 31% to $k_{obs} = 0.0124 \text{ hr}^{-1}$. Repeating this calculation with the [•OH]ss value for OWCFA yields a rate constant of 7.9×10^{-3} hr⁻¹ or just under half of the photolysis rate constant ($k_{obs} = 0.0175 \text{ hr}^{-1}$). An OWC FA experiment run in the presence of isopropanol decreased degradation by 23% as can be seen in Figure 2.4, with a k_{obs} of 0.0134 hr⁻¹. The significant discrepancy between the observed amount of quenching and the calculated rate constant due to •OH for OWCFA cannot be explained at this time. In any case, these observations reinforce that •OH is a significant ROS promoting metolachlor degradation. Also shown in Figure 2.4 are the kinetics for the suboxic (anoxic) OWCFA experiment. As can be seen, the sub-oxic experiment is not statistically different from the OWC FA experiment so both sets of kinetics are fit to the same line for greater clarity in the figure. The isopropanol quenched experiment is

significantly slower than both the fulvic acid and the sub-oxic experiments.



Figure 2.4 The effect of isopropanol quenching on photo-degradation of metolachlor is shown by the solid triangles. The argon purged sub-oxic OWC FA experiment is shown by open circles and the air saturated experiment is shown by solid squares. These kinetics are not corrected for light screening.

2.3.3 The Role of Nitrate

A constituent other than DOM commonly found in surface waters and known to produce significant quantities of •OH upon irradiation is nitrate (Miller and Chin 2005). Although it has been shown to be an important sensitizer at concentrations of 1.0 mM, previous research has not well-demonstrated the lower limit of nitrate's dominance as a sensitizer. (Miller and Chin 2002) For this reason, we chose to examine the reactivity of a range of concentrations from 0 mM to 1mM nitrate. As can be seen in Figure 2.5, metolachlor degrades significantly faster in solutions spiked with nitrate. The addition of 0.2 mM NO_3^- increased the rate of degradation by 85.6%, 0.5 mM NO $_3^-$ increased the rate by 143.1%, and 1.0 mM NO $_3^-$ nearly tripled the rate of degradation. The addition of OWC FA to nitrate spiked solutions did not further increase the rate of degradation. For solutions of OWC FA, 0.2mM NO $_3^-$ increased the rate of degradation by 78.4%, 0.5mM NO $_3^-$ increased the rate by 142.4%, and 1.0mM NO $_3^-$ doubled the rate of degradation as compared to direct photolysis. These rates are considerably higher than the photolysis reactions that only contained fulvic acid or whole water. Thus, for metolachlor NO $_3^-$ is a much more important sensitizer of •OH formation than DOM. In addition, as •OH is the primary radical species generated by NO $_3^-$, these results suggest that •OH is the most important radical responsible for the degradation of metolachlor.



Figure 2.5 Metolachlor observed pseudo first order photo-degradation rate constants, k_{obs} , for direct photolysis (in deionized water) and photolysis in the presence of nitrate at various levels ranging from 0mM (Direct) to 1.0 mM. Grey striped bars represent experiments conducted with approximately 6 mg C/L Old Woman Creek Fulvic Acid (OWC FA) and various levels of nitrate, white striped bars represent experiments conducted in deionized water with nitrate, and the solid white bar represents photolysis in deionized water without nitrate. These rate constants are corrected for light screening and are reported at the 95% confidence interval.

2.3.3 Photo-Fenton Pathway

The photo-Fenton pathway can be important for the degradation of surface water contaminants via the production of •OH. However, we chose not to explore the role of iron in the degradation of metolachlor. This is due to the fact that there was no decrease in the rate of reaction upon argon sparging of the OWC whole water, which excludes the possibility of the photo-Fenton pathway. Anoxic conditions prevent the formation of H_2O_2 which is necessary for the photo-Fenton pathway to occur. The whole water sample contained 0.021mM iron and while this is not high, it is sufficient that an effect should have been seen upon argon sparging if the photo-Fenton pathway was significant. Thus, iron is assumed to play only a minor role in the degradation of metolachlor under the conditions studied here.

2.3.4 Low Concentration Study

Previous studies of contaminants at low concentrations have demonstrated the potential for increased rates of degradation through the action of longer lived excited state species (Canonica and Freiburghaus, 2001). At higher contaminant concentrations, such as the 65 μ M metolachlor we examined, the dominant reactive pathways are likely to be via short lived excited state species, such as ³DOM or •OH. (Canonica and Freiburghaus, 2001) Indeed, photolysis experiments of metolachlor at an environmentally relevant concentration (0.5 μ M) indicate that reactions proceed more quickly for all of the fulvic acids. The greatest effect was observed for SRFA (71% faster) followed by OWC FA (37% faster) and finally PLFA (25% faster) as shown in

Figure 2.6. Even direct photolysis is 27% faster at 0.5 μ M metolachlor.



Concentration of Metolachlor (uM)

Figure 2.6 Low concentration observed pseudo first order rate constants for direct (in deionized water) photolysis of metolachlor and photolysis in the presence of fulvic acids. The low concentration experiments are represented by the gray bars (0.5 μ M) while white bars represent higher concentration (65 μ M) photolysis experiments. These rate constants are corrected for light screening and are reported at the 95% confidence interval.

Such marked changes in reactivity indicate a significant change in the mode of reaction. Specifically, it indicates longer lived excited state species (lifetime >2 μ s) become important species in the degradation of metolachlor. These longer-lived species

are acting in addition to the short-lived excited state species responsible for degradation at higher contaminant concentrations. The most likely reactive species responsible for degradation at low contaminant concentrations are peroxyl radicals as they have lifetimes on the order of seconds whereas •OH has a lifetime of ~ 1 μ s. At higher concentrations of contaminant, these longer lived species are scavenged by the contaminant itself (Canonica and Hoigné, 1995). Since direct photolysis is also faster at lower concentrations, it is possible that at 65 μ M metolachlor is self-quenching.

For each of the fulvic acids examined, reactivity increases with decreased metolachlor concentration. However, the extent of the effect differs depending on the fulvic acid source. It appears that at lower contaminant concentrations, terrestrial DOM, such as SRFA, plays a more significant role in metolachlor degradation. It appears that at low concentrations of metolachlor (<1 μ M) the composition of the DOM and, therefore, its origin becomes pertinent to degradation. The 0.5 μ M experiments examined here are still an order of magnitude higher than the 0.02 μ M concentrations of metolachlor found in the environment (Kolpin, 1998). Thus, it is possible that at 0.02 μ M, degradation of metolachlor is even faster, but such concentrations are below our current methods of analytical detection.

In order to determine the importance of •OH at low concentrations of metolachlor, a quencher was added to fulvic acid photolysis solutions. As can be seen from Table 2.2, addition of 25 mM isopropanol to 0.5 μ M metolachlor solutions in fulvic acid yielded degradation rate coefficients lower than that observed for 0.5 μ M direct photolysis. The order of reactivity was PLFA < OWC FA < SRFA. Degradation was quenched by 37% for OWCFA and by 53% for both SRFA and PLFA. This indicates that •OH is an important reactive transient, but it also suggests that at this concentration isopropanol may be quenching excited state metolachlor or other radical transients, as well.

				w/25mM isopropanol	
DOM	[DOC] (mg/L)	k _{obs} (hr⁻¹)	half-life (hr)	k _{obs} (hr⁻¹)	half-life (hr)
Direct		$(1.94 \pm 0.1) \times 10^{-2}$	35.7	not applicable	35.7
SRFA	6.43	$(3.34 \pm 0.5) \times 10^{-2}$	20.8	$(1.58 \pm 0.1) \times 10^{-2}$	43.9
OWCFA	6.335	$(2.40 \pm 0.1) \times 10^{-2}$	28.9	$(1.51 \pm 0.1) \times 10^{-2}$	45.9
PLFA	6.244	$(2.53 \pm 0.3) \times 10^{-2}$	27.4	$(1.19 \pm 0.2) \times 10^{-2}$	58.2

Table 2.2 Pseudo-First-Order Rate Coefficients for $0.5 \,\mu$ M Metolachlor ± 1 SD.

As with the higher concentration scavenging experiments, we can compare this data to calculations of the role of •OH in the degradation of metolachlor. Using the reported second order rate constant for metolachlor ($k_{\cdot OH}$) with •OH, 9.1 x 10⁹ L/mol-s (Wu et al., 2007) we can estimate the pseudo first-order rate constant (k'):

$$\mathbf{k}' = \mathbf{k}_{\bullet OH} \mathbf{x} \left[\bullet OH \right]_{ss} \tag{4}$$

where $k_{\cdot OH}$ is the second order rate constant and $[\bullet OH]_{ss}$ is different for each fulvic acid examined. The value for OWCFA was measured in our lab (using the method of Zhou and Mopper, 1990) and found to be 2.4×10^{-16} mol/L (Houtz, 2007). The calculated first order rate constant is 7.9×10^{-3} hr⁻¹ which corresponds to one third of the observed rate constant ($k_{obs} = 0.0240$ hr⁻¹). The $[\bullet OH]_{ss}$ value for SRFA is 2.9×10^{-16} mol/L. Thus the corresponding pseudo-first-order rate constant becomes 9.5×10^{-3} hr⁻¹ or just under a third of the observed rate constant for SRFA ($k_{obs} = 0.0334$ hr⁻¹). For PLFA,

the $[\cdot OH]_{ss}$ value is 8.8×10^{-17} mol/L, which leads to a pseudo-first-order rate constant of 2.9×10^{-3} hr⁻¹ or just over 10% of the observed rate constant for PLFA. The addition of 25 mM isopropanol quenched the reactions much more than would be anticipated by these calculations. In fact, the addition of isopropanol quenched the reactions to below the level of direct photolysis. This indicates that there may be side reactions in addition to •OH, which would be responsible for the increased rate of degradation at lower concentration.

2.4 Conclusions

Direct photolysis is a significant degradation pathway for metolachlor in surface waters at both 0.5 and 65 μ M. It is especially important that photolysis is an effective degradation pathway at 0.5 μ M as this approximates the concentration at which it is found in the natural environment. OWCWW and the three fulvic acid isolates examined increase the degradation rate compared to direct photolysis. While Pony Lake and Suwannee River fulvic acids are more reactive than Old Woman Creek fulvic acid or whole water, there is not a significant difference in reactivity among the three sources of DOM at 65 μ M metolachlor. Instead, nitrate sensitized •OH becomes a significant reaction pathway for metolachlor degradation at [NO₃⁻] > 200 μ M.

In addition, photolysis experiments conducted at environmentally relevant concentrations demonstrated that decreasing the concentration of metolachlor significantly increased the rate of degradation. Such a result indicates the formation of a long lived excited state species (Canonica and Freiburghaus, 2001). The most likely species is an organic peroxyl radical which is a longer lived species than ³DOM or •OH. In addition, at 0.5 μ M metolachlor the source of the DOM becomes relevant with SRFA increasing the rate of degradation significantly more than PLFA or OWCFA. Isopropanol quenching experiments indicate that at low concentrations of metolachlor additional reactions may be occurring.

CHAPTER 3

PHOTOCHEMICAL TRANSFORMATION OF TRICLOCARBAN

3.1 Introduction

There are a variety of ways in which environmentally relevant contaminant species can be introduced to surface waters. Household chemicals and pharmaceuticals can be introduced through wastewater treatment plants, septic systems, leaking sewerage systems, or sanitary or combined sewer overflows. Another important source of contaminants is activated sludge. In the case of triclocarban, activated sludge accounts for the introduction of at least 5800 kg to surface waters annually (Halden and Paull, 2005). The presence of household chemicals and pharmaceuticals in surface waters is of concern due to the possible formation of toxic by-products, toxicity and persistence of the chemicals themselves, or hormonal activity of the compounds (Kolpin et al., 2002).

While point sources are generally monitored by the U.S. EPA, an important exception is the number of micropollutants found in the effluent of wastewater treatment plants (WWTP). Among these are pharmaceuticals and personal care products (PPCPs) that are introduced to wastewater streams but are not degraded in wastewater treatment plants. In large cities with considerable household inputs, the concentrations of these compounds can become significant. In addition, it has recently been observed (Heidler et al., 2006) that sewage sludge can contain significant quantities of PPCPs. For example, approximately 97% of triclocarban entering a WWTP will sorb to particulate matter (Heidler et al, 2006). Since sewage sludge is often applied to agricultural land as fertilizer, this can often lead to surface water contamination in addition to that caused by WWTP effluent. When present in biosolids used as field amendments, triclocarban has been shown to persist in runoff waters for up to 266 days after the initial application (Chu and Metcalfe, 2007). Thus, the use of triclocarban in PPCPs introduces this chemical to the natural environment in significant quantities.

3.1.1 Environmental Fate of Triclocarban

Triclocarban is considered a high production volume chemical with 500,000 – 1,000,000 pounds of it produced annually in the United States (Halden and Paull, 2005). It is used in PPCPs such as soaps, creams, and cosmetics to prevent spoilage and bacterial growth. It has been used commercially in the U.S. since 1957, but few studies have been conducted to assess its toxicity and transport in the environment. This is surprising considering the related compound triclosan has been the subject of over 2,000 peer reviewed studies. However, this lack of previous investigation makes the determination of the fate of this environmental toxicant even more important.

Triclocarban is soluble in organics and readily crosses cell membranes, as can be predicted by its high octonal-water partitioning coefficient, (Kow = 4.9). It is also fairly recalcitrant with an estimated half-life of 120 days in soil and 540 days in sediment

(Heidler et al., 2006). For these reasons, it can be considered quite biologically active within an ecosystem. Triclocarban is known to interfere with mammalian reproduction and cause methemoglobinemia, or reduced oxygen affinity of hemoglobin, in humans (Halden and Paull, 2005). It also amplifies the natural action of androgens and may possibly impact the use of hormones for birth control and hormone replacement therapy in human females (Chen et al., 2008). Triclocarban is thought to be a potential carcinogen due to the possibility of carbon-nitrogen bond cleavage which would generate N-hydroxylated metabolites. In addition, triclocarban yields mono- and dichlorinated anilines as degradation by-products in the environment. These compounds are hematotoxic, genotoxic, and persistent (Halden and Paull, 2005). Finally, as an antimicrobial agent it has the potential to contribute to the formation of resistant forms of bacteria. Due to its many potential sources of toxicity, triclocarban is of serious concern as a surface water pollutant.

In this research, it was our aim to investigate the photolytic degradation of triclocarban. To this end we performed direct photolysis experiments in de-ionized water as well as fulvic acid and whole water experiments. We also performed DOM experiments in the presence of 20 μ M iron to ascertain the importance of the photo-Fenton pathway. Three fulvic acids were chosen to represent a spectrum of possible reactivity – from an autochthonous end member composed of microbial and algal derivatives to an allochthonous end member composed of terrestrial plant derivatives. As with metolachlor, the autochthonous endmember came from Pony Lake, Antarctica which is completely free of inputs from higher plants. The allochthonous endmember is

from the Suwannee River in GA, USA, an acidic blackwater swamp. An additional sample representing a mixture of autochthonous and allochthonous material is represented by Old Woman Creek, an estuary feeding into Lake Erie in Huron, OH. A whole water sample was also taken from Old Woman Creek to represent the full portion of DOM instead of only the fulvic acid fraction. It was our intention to investigate to what extent the chemical differences among the three fulvic acids would impact the degradation kinetics of triclocarban.

3.2 Materials and Methods

3.2.1 Chemicals and Reagents

Materials. All chemicals and reagents were purchased commercially and used without further purification. Chemicals and reagents were acquired from the following: Triclocarban (99.5%) from Chem Services West Chester, PA; methanol (Optima), acetonitrile (Optima), sodium hydroxide (NaOH; analytical reagent) from Mallinckrodt; potassium hydrogen phthalate (KHP), sodium nitrate, *p*-nitroanisole, and pyridine from Aldrich (Milwaukee, WI); AG-50W-X8 resin from Bio-Rad (Hercules, CA); argon (4.8 grade) from Praxair. The reference fulvic acids Suwannee River Fulvic Acid (SRFA) Lot #1R101F-1 and Pony Lake Fulvic Acid Lot #1R109F were purchased from the International Humic Substance Society (IHSS). All glassware was washed with NOCHROMIX Cleaning Reagent (Godax Laboratories, Inc) in concentrated sulfuric acid and all plastics were washed with 10% HCl prior to use.

3.2.2 Dissolved Organic Matter Isolates and Wetland Water

Natural organic matter XAD-8 isolates were chosen to represent a spectrum of reactivity. *Suwannee River Fulvic Acid (SRFA)* This organic matter is rich in materials external to the water column, and the water exhibits minimal primary productivity within the water column. These qualities serve to make the fulvic acid an allochthonous, or terrestrial endmember on the fulvic acid spectrum.

Pony Lake Fulvic Acid (PLFA) The source, Pony Lake, is located in Antarctica and receives no terrestrial inputs as there are no higher land plants on the continent. Thus, it is rich in algal and microbial organic matter constituents derived within the water column and so is an autochthonous fulvic acid endmember.

OWC Fulvic Acid (OWC FA) This was isolated in our lab according to standard protocols. Old Woman Creek (OWC) is a temperate eutrophic wetland located on the south shore of Lake Erie. We isolated the fulvic acid fraction of OWC DOM by adsorption to non-ionic XAD-8 resin under acidic (pH 2) conditions, elution under alkaline conditions (pH 10), and deionization with Amberlite AG-50 cation exchange resin (H+-saturated) according to established protocols (Leenheer, 1981; Thurman and Malcolm, 1981). The solution was then freeze-dried and stored at room temperature until use.

3.2.3 Photolytic Reactions

Reaction mixtures were prepared according to the following procedure. A stock solution of triclocarban was prepared in methanol. From this stock solution, photolysis

solutions were prepared by evaporating an aliquot of stock and reconstitution in the appropriate matrix. (Milli-Q or fulvic acid). Final concentrations were 0.5 μ M triclocarban and 4.5-5.0 mg C/L DOC. To probe the role of hydroxyl radical, photolysis experiments with excess methanol (25mM) as an •OH scavenger were performed. Sub-oxic experiments were purged with argon for 90 minutes (1min/mL) and transferred to quartz tubes in a glove box under a 95% N₂/ 5% H₂ atmosphere.

In all cases, solutions were irradiated in air-tight quartz tubes sealed with Teflon caps with no headspace. Photolysis experiments were performed in a CPS+ Solar Simulator (Atlas Electric Devices) with an 1100 watt xenon arc lamp. By using an H filter, the "Solar standard" filter, the output of the simulator is able to mimic the spectrum of natural sunlight for wavelengths from 290 to 800 nm. Initial pH was 7.0 and was constant over the course of the reaction. Dark controls were run concurrently for each photolysis experiment. Temperature was measured using a black standard temperature (BST) probe set to 25°C. Kinetic data was fitted to a pseudo-first order equation. Irradiation experiments were carried out for 24 hours, with samples sacrificed every three hours for High Pressure Liquid Chromatography (HPLC) analysis to determine loss of the parent compound. A direct aqueous injection (200uL) was made from each vial into the HPLC and separation was achieved using a Novapak Waters C-18 reverse-phase chromatography column and detected using a Waters 2487 dual λ Absorbance detector at 257nm. Mobile phase for the analysis was 80% methanol / 20% Milli-Q (v/v) and the flow rate was 1.0 mL/min. Kinetic data were analyzed using Microsoft Excel and SigmaPlot 10.0. Rate coefficients for metolachlor degradation were determined using a

least-squares fit of the observed data to a pseudo-first order kinetics model with $R^2 > 0.97$ for all reactions.

In order to monitor photon flux and to check for changes in the light intensity of the lamp, chemical actinometry was conducted periodically using the p-nitroanisole (PNA)/pyridine (PYR) system (Dulin and Mill, 1982). Over the course of this research, no significant changes in light intensity were observed. The following equation is used to compare reaction rates between the solar simulator and natural sunlight using PNA's equivalent rate constant (k) at solar noon in June at 40° N, (the approximate latitude of Columbus, Ohio):

$$\mathbf{k} = \phi_{\lambda} \sum \varepsilon_{\lambda} \Lambda_{\lambda} \tag{1}$$

where ϕ is PNA's quantum yield, ε is the molar absorption coefficient of PNA, and Λ is sunlight irradiance for a specific wavelength (Leifer, 1988). Due to a change in lamp, the rate constant for this set of data was different from that calculated for the metolachlor data set and was calculated to be 3.1 times faster in the simulator. Thus, the triclocarban degradation rates presented here are significantly faster than would be observed in natural sunlight due to the intensity of the light source used. Other factors including surface scattering of incident light and attenuation within the water column would further slow kinetics in a natural setting as compared to the presented results. However, these phenomena would presumably only serve to slow the kinetics, not alter the relevant degradation pathways.

3.3 Results and Discussion

3.3.1 Reaction Kinetics

The absorbance spectrum of triclocarban is shown in Figure 3.1 and indicates sufficient absorption above 290 nm that direct photolysis would be predicted. Indeed, direct photolysis of triclocarban was observed in Milli-Q at a concentration of 0.5 μ M with a measured half-life of 24 hours in the solar simulator. Assuming eight hour days, this corresponds to three full days of photolysis in summer sunlight. Dark controls were run concurrently for all experiments, but under all conditions examined dark reactions were not observed. This confirms that the degradation kinetics observed are due to exclusively photolytic pathways.



Figure 3.1. Absorbance spectrum of triclocarban normalized to $\lambda = 257$ nm.

In order to probe the reactivity of a spectrum of fulvic acids, experiments were run in the presence of SRFA, OWCFA, and PLFA as well as OWCWW. The degradation rate constants are shown in Table 3.1 and Figure 3.2. As can be seen, the presence of any of the three fulvic acids tested as well as the whole water increases the rate of degradation. For OWC FA the observed rate constant (k_{obs}) is $k_{obs} = 0.0464$ hr⁻¹, for SRFA $k_{obs} = 0.0364$ hr⁻¹, for PLFA $k_{obs} = 0.0508$ hr⁻¹, for OWC whole water $k_{obs} = 0.0405$ hr⁻¹. Thus, the rate of degradation increased by 27.3% for SRFA, 62.2% for OWC FA, 77.6% for PLFA, and 41.6% for OWC whole water compared to direct photolysis. The half-life for each rate coefficient is also given in Table 3.1 and, assuming an 8-hr irradiation period, these half-lives translate to 1.7 (for PLFA) – 3.0 (for direct) days of summer sunlight.

DOM	[DOC] (mg/L)	k _{obs} (hr⁻¹)	Σ S ₂₉₀₋₃₇₅	Fe _T	[NO₃ ⁻]	half-life (hr)
Direct		$(2.86 \pm 0.3) \times 10^{-2}$				24.2
OWC WW	4.834	(4.05 ± 0.4) x 10 ⁻²	0.92	0.021mM	0.071mM	17.1
SRFA	4.972	(3.64 ± 0.3) x 10 ⁻²	0.91			19.0
OWCFA	4.935	(4.64 ± 0.5) x 10 ⁻²	0.92			14.9
PLFA	4.692	$(5.08 \pm 0.3) \times 10^{-2}$	0.92			13.6

Table 3.1	Pseudo-First-	Order Rate	Coefficients	for Photo	lysis of	Tricloca	$rban \pm 1$	SD.
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As discussed in Chapter 2, there is expected to be a significant difference in the chemical composition of the three fulvic acids and a possibility for considerable variability in reactivity towards contaminants. In the case of triclocarban, this is indeed what is observed – the two end members exhibit very different reactivity with Old Woman Creek fulvic acid and the whole water falling in between the two extremes. The

order of reactivity with triclocarban is PLFA \geq OWC WW > OWC FA > SRFA. This indicates that microbially derived DOM is significantly more reactive towards triclocarban than terrestrially derived DOM. Microbial DOM has previously been shown to be more reactive than more aromatic terrestrial DOM in the degradation of bisphenol A (Chin et al., 2004). Additionally, as with metolachlor, the extent to which OWC whole water increases the rate of photolysis is statistically the same as for the OWC fulvic acid. This supports the assumption that the fulvic acid fraction is the most photo-active portion of the DOM and therefore the most experimentally relevant.

In addition to sensitizing photolysis, DOM can preferentially absorb photons, decreasing the photons available to initiate contaminant degradation creating an effect known as light screening. This process occurs through the action of chromophores, or light absorbing moieties within the DOM structure. In order to quantify such light screening in the whole water and fulvic acid solutions, we applied a correction factor that was calculated for each rate constant. Using a UV-Vis absorbance scan for each sample, a light screening factor is calculated for each wavelength according to the following equation:

$$S_{\lambda} = [1 - 10^{-(1.2)(A)}] / (2.3)(1.2)(A)$$
(2)

where A is absorbance, 1.2 is an average distribution function of light in natural waters, (Schwarzenbach et al., 2003; Zepp and Cline 1977) and $S_{\lambda} = 1.0$ if no attenuation by DOM occurs. We plotted S_{λ} versus wavelength and integrated the area under the curve to determine the overall screening factor over the wavelengths of interest (290 to 350 nm), the region in which DOM has the highest absorption. The OWC FA solution has a screening factor of 0.92, the SRFA solution has a screening factor of 0.91, the PLFA solution has a screening factor of 0.92, and the OWC whole water has a screening factor of 0.92. The impact of fulvic acid on degradation rate corrected for light screening is shown in Figure 3.2. The corrected rate constants are ($k_{corrected} = 0.0396$) for SRFA, ($k_{corrected} = 0.0504$) for OWC FA, ($k_{corrected} = 0.0552$) for PLFA, and ($k_{corrected} = 0.0445$) for OWC WW. As can be seen from the 95% confidence intervals in Figure 3.1, the degradation rate constant observed in PLFA solution is significantly faster than both SRFA and OWCFA. The OWCWW rate is not statistically different from that for PLFA.



Figure 3.2. Triclocarban observed pseudo first order photo-degradation rate constants, k_{obs} , for direct photolysis (in deionized water) and photolysis sensitized by fulvic acids. These rate constants are corrected for light screening and are reported at the 95% confidence interval.

3.3.4 Argon Sparged Reactions

To determine the mode of reactivity, experiments were conducted to identify the responsible reactive species. First, those species originating from DOM were explored. Excited-state DOM can react with oxygen (O_2) to form reactive oxygen species (ROS) that, in turn, react with triclocarban or triplet state DOM (³DOM) can react with ground state triclocarban through energy or electron transfer. In order to probe the potential for either of these mechanisms, a sub-oxic photolysis was performed for each of the fulvic acids and the whole water. Removal of O_2 from the bulk reaction mixture allows one to selectively remove ROS that require the presence of O_2 to form including singlet oxygen $(^{1}O_{2})$, peroxyl radical (ROO•), and superoxide (O_{2}^{-}). The kinetic data for PLFA are shown in Figure 3.3 – argon sparging significantly increases the rate of degradation as compared to a non-sparged PLFA solution. The rate constants for degradation are shown in Figure 3.4. In each case, the rate increased when the photolysis solution was sparged with argon prior to reaction. For OWCFA the rate of reaction was increased by 26%, for PLFA by 42%, for SRFA by 54%, and for OWCWW by 56%. This indicates that ³DOM plays a significant role in triclocarban degradation.

Possible ³DOM reaction pathways include energy or electron transfer, hydrogen abstraction, or the formation of hydrated electron $e_{(aq)}^{-}$. However, energy transfer from DOM to triclocarban is unlikely as this would require the excited state of triclocarban to be lower in energy than the energy level of ³DOM. Instead, it is to be expected that the excited state of triclocarban is higher in energy than ³DOM.

The observed increases in reaction rate demonstrate a marked difference in reactivity for OWCFA, which appears to be much less dependent on a ³DOM pathway than the whole water or the other two fulvic acids. This correlates well with the slower overall reaction rate observed for OWCFA versus the other DOMs examined. However, I cannot offer an explanation for this difference in reactivity. The rate of degradation increased significantly for SRFA and PLFA indicating that ³DOM is essential to the reactivity of both of these fulvic acids.



Figure 3.3. Degradation kinetics of triclocarban showing the effect of argon sparging the photolysis solution for 1.5 hrs before photolysis. Removing O_2 from the bulk reaction solution increased the rate of triclocarban degradation by 42%.

In addition to illustrating ³DOM reactivity, the argon sparging experiments provide important information about the role of ROS in triclocarban degradation. Since argon sparging did not diminish the rate of triclocarban degradation, it can be surmised that singlet oxygen ($^{1}O_{2}$), peroxyl radical (ROO•), and superoxide (O_{2}^{-}) are not primary reactive transients leading to degradation. These ROS require the presence of O_{2} in the bulk reaction solution to form and so are not generated under sub-oxic conditions. Another possibility is that ROS do contribute to triclocarban degradation, but under suboxic conditions the ³DOM pathway obscures the importance of ROS formation. It is still possible that hydroxyl radical plays a significant role in the degradation of triclocarban, however, and this can be investigated with a straightforward scavenging experiment.



Figure 3.4. Degradation rate constants (k_{obs}) for direct photolysis (in deionized water) and sub-oxic (argong sparged) DOM experiments. These rate constants are reported at the 95% confidence interval.

3.3.5 Methanol quenching

In order to examine the role of •OH in the degradation of triclocarban, fulvic acid experiments were run in the presence of an •OH scavenger, 25mM methanol. In the case of each experiment, the rate of degradation decreased with the addition of scavenger. Specifically, the decrease was 29% for PLFA, 28% for OWC FA, 22% for SRFA, and 18% for OWC WW. This observation indicates that •OH is an important reactive transient promoting triclocarban degradation. Figure 3.5 illustrates kinetics generated by the addition of 25 mM methanol to a solution of PLFA. The methanol quenched rate constants for all of the DOMs are shown in Figure 3.6 in comparison to direct photolysis. The significant amount of quenching observed indicates that DOM sensitized formation of •OH can explain a large portion of the increase in rate of degradation due to whole water and the fulvic acids.



Figure 3.5. Degradation kinetics of triclocarban showing the influence of the addition of 25 mM methanol to a PLFA solution.

In the case of SRFA, the addition of methanol quenched the reaction to the rate of direct photolysis indicating that •OH is likely the most important DOM mediated pathway occurring for this fulvic acid. OWCWW and OWCFA were also essentially quenched by the addition of methanol. However, PLFA reacted 25% faster than direct photolysis when quenched with methanol. This indicates that for PLFA DOM undergoes reactive pathways in addition to •OH production. These pathways can include ³DOM, energy or electron transfer, hydrogen abstraction, or formation of aqueous electron.



Figure 3.6 Degradation rate constants (k_{obs}) for direct photolysis (in deionized water) and methanol quenched DOM reactions with triclocarban. These rate constants are reported at the 95% confidence interval.

3.3.6 Photo-fenton Reaction

As described in the introduction, it is possible for the presence of iron in natural waters to catalyze contaminant degradation through the production of •OH. In order to examine the possibility of photo-Fenton induced degradation of triclocarban, we spiked fulvic acid solutions with 20 μ M FeCl₃. For SRFA, the k_{obs} = 0.0231 hr⁻¹, for OWCFA k_{obs} = 0.0296 hr⁻¹, and for PLFA k_{obs} = 0.0258 hr⁻¹. As can be seen in Figure 3.7, none of these rate coefficients is significantly faster than direct photolysis of TRICLOCARBAN. Surprisingly, the rate of degradation actually decreased for both SRFA and PLFA. The reason for this somewhat anomalous result has yet to be determined.



Figure 3.7 Degradation rate constants (k_{obs}) for triclocarban direct photolysis and for fulvic acid solutions spiked with 20 μ M of FeCl₃.

3.4 Conclusions

Direct photolysis is a significant degradation pathway for triclocarban. OWCWW and all three of the fulvic acid isolates examined increase the degradation rate compared to direct photolysis. Pony Lake fulvic acid is the most reactive of the three fulvic acids examined and appears to react by both a ³DOM pathway and via the production of •OH. Old Woman Creek fulvic acid is the least reactive and appears to be less dependent on a ³DOM pathway. Suwannee River fulvic acid demonstrated a median level of reactivity and seems to depend on a combination of ³DOM and •OH pathways. The photo-Fenton pathway is not significant for any of the three fulvic acids.

CHAPTER 4 CONCLUSIONS

4.1 Summary of Results

Source of DOM. This research found that under certain conditions the source of DOM has a statistically significant influence on the rate of contaminant degradation. In the case of metolachlor the influence of the source of DOM was found to vary. At high concentrations (65 μ M), the source of DOM did not influence the rate of degradation while at low (0.5 μ M) concentrations terrestrially derived organic matter was found to enhance reactivity significantly more than microbially derived organic matter. In the case of triclocarban, microbially derived organic matter. This affirms the hypothesis that DOM is structurally and chemically different depending on its origin and that these differences have important effects on reactivity towards contaminant molecules. The fact that the order of reactivity for the fulvic acids is opposite for the two compounds indicates that DOM reactivity is compound-dependent.

Reaction pathways. For both compounds, direct and sensitized photolysis are significant pathways for contaminant removal from surface waters. Also for both compounds, dark reactions were found to be insignificant. The increase in the rate of

degradation upon the addition of DOM indicates that a sensitized pathway occurred. In order to probe the mechanistic details of this pathway, an •OH scavenger was employed. Isopropanol was used as the scavenger in the case of metolachlor while methanol was used in the case of triclocarban. In each case, the photolysis reaction was quenched by approximately 20-30% indicating that •OH plays an important role in the sensitized degradation of both compounds.

DOM is not the only possible source of •OH in surface waters. Indeed, nitrate sensitized •OH production becomes the primary reactive pathway for metolachlor degradation at $[NO_3^-] > 200\mu M$. In addition, photolysis experiments conducted at environmentally relevant concentrations of metolachlor demonstrated that decreasing the concentration significantly increased the rate of degradation. Such a result indicates the formation of a long lived excited state species. More investigation is required to identify this species. It is possible that an organic peroxyl radical is responsible for the increased rate of degradation as peroxyl radicals are known to be long lived species. Faust and Hoigne (1987) showed that 2,4,6 – trimethylphenol (TMP) can be used as a probe molecule for organic peroxy radicals as it is highly reactive towards them. Thus, TMP spiked experiments could be performed to further elucidate the reaction mechanism of metolachlor at low concentration.

Argon sparging experiments were performed to evaluate the importance of triplet DOM (³DOM) and reactive oxygen species (ROS). The purpose of argon sparging is two-fold – by removing oxygen from the system, ROS other than •OH can no longer form. In addition, O_2 is the most important quencher of ³DOM – by removing it, any
³DOM pathway will be significantly enhanced. In the case of metolachlor, argon sparging had no significant impact on the rate of degradation indicating that neither ³DOM nor ROS other than •OH play an important role in degradation. However, in the case of triclocarban, argon sparging significantly increased the rate of degradation. This signifies that while ROS other than •OH are not important, ³DOM does play a significant role in the degradation pathway of triclocarban.

4.2 Environmental Significance

This research indicates that both compounds will degrade significantly in surface waters. Naturally occurring water constituents including nitrate and DOM would increase the rate of degradation, while iron and the photo-Fenton reaction seem to be insignificant. In the case of metolachlor, degradation would be fastest in agricultural waters that contain high levels of nitrate. This is likely also true for triclocarban. In any case, wetlands provide conditions well-suited to contaminant degradation as they allow considerable light penetration throughout the water column and simultaneously provide chemical species that can sensitize degradation via the production of highly reactive transients such as •OH.

4.3 Future Work

A complete understanding of the environmental fate of metolachlor and triclocarban would require further investigation. Kolpin et al. (1996), Phillips et al. (1999), and Rebich et al. (2003) showed that metabolites of a contaminant are frequently

detected at higher concentrations than the parent compound. Thus, determining the photolysis by-products of both metolachlor and triclocarban would be essential to developing a complete model of their environmental fate. Ideally, toxicity of each by-product would also be evaluated. Performing photolysis experiments for both compounds in natural sunlight would confirm the estimated half-lives and more accurately approximate real world degradation kinetics.

In order to more fully evaluate the reaction mechanism for triclocarban, it would be important to determine which ³DOM pathway is occurring as there are several possibilities. ³DOM can undergo energy or electron transfer, it can sensitize •OH production, or it can produce hydrated electrons e⁻_(aq). A triplet energy sensitizer such as perinaphthenone should be used to evaluate the possibility of triplet energy transfer versus •OH production. It would also be valuable to estimate the pseudo-first-order rate constant between •OH and triclocarban. In order to do this, the second order rate constant of triclocarban and •OH would need to be measured. In addition, while it can readily be predicted that nitrate would increase the rate of degradation of triclocarban through increased production of •OH, experiments should be conducted to confirm this assumption.

A broader aim of this research was to evaluate the importance of DOM source in the degradation of synthetic organic contaminants. In order to more fully understand the relationship of DOM source to its reactivity, more contaminant compounds need to be evaluated. Using compounds with various functional groups and allowing them to be sensitized by a spectrum of DOM would help to determine which compounds are more reactive with microbially derived DOM and which compounds are more reactive with terrestrially derived DOM. Such information could considerably improve remediation methods.

APPENDIX A

UV-VIS SPECTRA



Figure A.1. UV-vis spectrum of Suwannee River fulvic acid (SRFA).



Figure A.2. UV-vis spectrum of Old Woman Creek fulvic acid (OWCFA).



Figure A.3. UV-vis spectrum of Pony Lake fulvic acid (PLFA).



Figure A.4. UV-vis spectrum of 1.0 mM NaNO₃ solution normalized to $\lambda = 215$ nm.

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