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PHOTOCHEMICAL TRANSFORMATION OF AGRICULTURAL PESTICIDES
PROMOTED BY NATURAL WATER CONSTITUENTS IN WETLAND
SURFACE WATERS

DISSERTATION

Presented in Partial Fulfillment of the Requirements
for the Degree Doctor of Philosophy in the
Graduate School of The Ohio State University

By
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* * * * *

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2001

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ABSTRACT

Non-point source (NPS) pollution from surface runoff contaminated with agrochemicals is a major environmental concern. Photolysis is an important degradative pathway for many agrochemicals and can occur through direct and indirect pathways. Wetlands, especially those receiving agricultural drainage, may be rich in constituents such as natural organic matter (NOM) and total nitrates (nitrate + nitrite) which are capable of promoting the transformation of organic compounds via indirect photochemical pathways. The goal of this research is to learn if the photochemical processes occurring in freshwater wetlands located in agricultural watersheds can improve water quality. Specifically, this research sought to elucidate how wetland water constituents would promote and inhibit direct and indirect photochemical processes. The objective of the research were: (1) to probe the ability of wetland water constituents to promote the photodegradation of "target" contaminants through indirect photolysis under environmentally relevant conditions (solar simulation); (2) to evaluate the direct and indirect photolytic contribution to "target" compound degradation; (3) to characterize the specific photoreactive constituents present in wetland water samples (natural organic matter (NOM) and/or inorganic anions and cations); (4) to identify the parameters that affect the process efficacy; (5) to ascertain the what the spatial and temporal variability
will be for these dynamic systems; and (6) to relate photochemical reactivity to measurable indices.

Water samples were collected from several wetland field sites located in agricultural watersheds and from the Suwannee River. Natural organic matter (NOM) isolates were also used from well-documented systems (Suwannee River and Lake Fryxell Fulvic Acids) for comparison. Characterization of water quality parameters (UV/VIS, TOC, IC) was performed on all tested water samples to identify potential photosensitizers. The “target” non-point source (NPS) pollutants, *i.e.*, carbaryl and alachlor, were chosen on the basis of their ubiquitous use in Ohio agriculture and their susceptibility to direct (carbaryl) and indirect (through its reaction with HO*) photolysis.

Photochemical experiments were conducted using a solar simulator. Reactions were carried out at the pH of the natural water sample and in samples whose pH’s were adjusted to ~4. Samples were assayed by either HPLC or GC/ECD for the parent compound and any detectable derivatives. Pseudo-first order degradation rate coefficients were determined from least squares fit of the observed kinetic data to serve as a measurable index of reaction efficiency to facilitate the comparison with other samples. When necessary, rate coefficients were corrected for the variation in source light intensity and inner filter effects.

At the ambient pH (~8) of these alkaline wetland waters, direct photolysis and a dark reaction were effective at degrading carbaryl but not alachlor. For both compounds, waters containing high levels of nitrate led to significant photodegradation through the photolysis of nitrate. At lower pH’s, the indirect photolysis, *i.e.*, due to the presence of
naturally occurring photosensitizers other than nitrate, increased significantly for both molecules. The promotion of the reactions at low pH is apparently related to the activation of certain photochemical pathways promoted by NOM and/or Fe-NOM complexes. Photobleaching studies provided support that indirect processes were promoted at low pH.

Moreover, the photoenhanced degradation at low pH was found to be seasonally and spatially dependent. A close correspondence between nitrate level and observed reaction rate coefficients is observed when nitrate levels are high in the wetland. However, little (<10%) of the indirect degradation observed in the latter season samples (low nitrate) could be attributed to nitrate photolysis, and corresponded well to the [TOC] and possibly trace levels of iron. Thus, the enhancement by light appeared to be related to three primary constituents: total nitrates, NOM, and iron.

The efficacy of indirect photolysis depended on the concentration of the natural photosensitizers and of ROS scavengers such as dissolved NOM and carbonate species. For the levels of TOC measured in these samples, the effect of carbonate species on scavenging was insignificant (<8%). Paradoxically, during low nitrate events (<50 µM), NOM becomes the principal photosensitizer either through the production of HO· and/or production of unidentified transient species. Contrary to results published for other carbamates (i.e., carbofuran) and alachlor, the reactivity of NOM did not correlate to its hydrophobicity. Certainly, a delicate balance exists between NOM's role as a photosensitizer and an intermediate scavenger.
DEDICATION

Dedicated to David
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I wish to thank God who through His sovereign will allowed me the opportunity and blessed me with the skills to pursue these studies.

I thank my husband, David, for his love and encouragement through these past years as I have pursued my doctorate.

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Science and Technology, 32, 1269-1275.

Nitroaromatic Compounds Related to Military Ordnance Constituents,”
Environmental Science and Technology, 30, 1192-1197.

FIELD OF STUDY

Major Field: Environmental Science
# TABLE OF CONTENTS

Abstract ............................................................................................................................ ii

Dedication ....................................................................................................................... vi

Acknowledgments.......................................................................................................... vii

Vita................................................................................................................................ viii

List of Tables ................................................................................................................. xiv

List of Figures ............................................................................................................... xvi

Chapters:

1. Introduction ............................................................................................................ 1
   1.1 Nature and Scope of the Research .................................................................. 1
   1.2 Photochemistry in Natural Waters ............................................................... 5
   1.3 Relationship of NOM Photochemistry to Contaminant Fate in Wetlands ........ 9
   1.4 Rationale for Present Research .................................................................. 14
   1.5 Research Goals ......................................................................................... 15
   1.6 Anticipated Results and Benefits .............................................................. 17

2. Photochemical transformation of carbaryl promoted by natural water constituents in a wetland surface water sampled from an agricultural watershed .......................................................... 20
   2.1 Introduction .............................................................................................. 20
   2.2 Material and Methods ................................................................................ 22
       2.2.1 Chemicals and Reagents .................................................................. 22
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2.2 Collection and Characterization of Wetland Raw Water</td>
<td>23</td>
</tr>
<tr>
<td>2.2.3 Photolytic Reactions</td>
<td>24</td>
</tr>
<tr>
<td>2.2.4 Fluorescence Lifetime Measurements</td>
<td>26</td>
</tr>
<tr>
<td>2.2.5 Data Analysis</td>
<td>28</td>
</tr>
<tr>
<td>2.3 Results and Discussion</td>
<td>28</td>
</tr>
<tr>
<td>2.3.1 Natural Water Characteristics</td>
<td>28</td>
</tr>
<tr>
<td>2.3.1.1 Light Screening Factors</td>
<td>31</td>
</tr>
<tr>
<td>2.3.2 Reaction Kinetics</td>
<td>33</td>
</tr>
<tr>
<td>2.3.3 Direct Photolysis</td>
<td>37</td>
</tr>
<tr>
<td>2.3.3.1 Effect of pH on the Direct Photolysis</td>
<td>40</td>
</tr>
<tr>
<td>2.3.3.2 Calibration of Photoreactor for Predicting Direct Photolysis</td>
<td>45</td>
</tr>
<tr>
<td>2.3.4 Indirect Photolysis</td>
<td>46</td>
</tr>
<tr>
<td>2.3.4.1 Total Nitrates</td>
<td>49</td>
</tr>
<tr>
<td>2.3.4.2 Natural Organic Matter</td>
<td>57</td>
</tr>
<tr>
<td>2.4 Conclusions</td>
<td>67</td>
</tr>
<tr>
<td>3. Effect of wetland water constituents on the photoinduced degradation of the herbicide</td>
<td>93</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>93</td>
</tr>
<tr>
<td>3.1.1 Environmental Fate of Alachlor</td>
<td>94</td>
</tr>
<tr>
<td>3.1.2 Goals for this Study</td>
<td>98</td>
</tr>
<tr>
<td>3.2 Methods</td>
<td>99</td>
</tr>
<tr>
<td>3.2.1 Materials</td>
<td>99</td>
</tr>
<tr>
<td>3.2.2 Water Samples and NOM Isolates</td>
<td>100</td>
</tr>
<tr>
<td>3.2.2.1 Collection and Characterization of Wetland Raw Waters</td>
<td>100</td>
</tr>
<tr>
<td>3.2.2.2 Characterization of Wetland Water samples</td>
<td>104</td>
</tr>
<tr>
<td>3.2.2.3 NOM Isolates</td>
<td>105</td>
</tr>
<tr>
<td>3.2.3 Photolytic Reactions</td>
<td>107</td>
</tr>
<tr>
<td>3.2.4 Actinometry and Light Intensity Corrections</td>
<td>109</td>
</tr>
<tr>
<td>3.2.5 ( \text{H}_2\text{O}_2 ) Measurement</td>
<td>110</td>
</tr>
<tr>
<td>3.2.6 Data Analysis</td>
<td>111</td>
</tr>
<tr>
<td>3.3 Results and Discussion</td>
<td>112</td>
</tr>
<tr>
<td>3.3.1 Analysis of Natural Water samples</td>
<td>112</td>
</tr>
<tr>
<td>3.3.2 Photolysis of Alachlor in Agricultural Wetland Waters</td>
<td>116</td>
</tr>
<tr>
<td>3.3.3 Identification of Potential Reactive Transients</td>
<td>126</td>
</tr>
<tr>
<td>3.3.4 Discussion</td>
<td>134</td>
</tr>
<tr>
<td>3.3.5 Role of NOM in Mediating this Reaction</td>
<td>142</td>
</tr>
<tr>
<td>3.3.6 Role of Hydrogen Peroxide</td>
<td>150</td>
</tr>
<tr>
<td>3.3.7 The pH Dependency</td>
<td>157</td>
</tr>
<tr>
<td>3.3.8 Role of Iron Mediating the Photodegradation of Alachlor</td>
<td>169</td>
</tr>
</tbody>
</table>
Appendices:

A  Absorbance Spectra and Kinetic Timecourses for the Carbaryl Study ............... 304
B  Absorbance Spectra and Kinetic Timecourses for the Alachlor Study ............... 321
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Water quality characteristics for water samples taken from Old Woman Creek (OWC) in June, August, and September of 1998. Values in parenthesis represent %CV for replicate samples.</td>
<td>69</td>
</tr>
<tr>
<td>2.2</td>
<td>Measured initial rate coefficients and total mass balances for the degradation of carbaryl in Old Woman Creek wetland water in the dark and light.</td>
<td>70</td>
</tr>
<tr>
<td>2.3</td>
<td>Measured fluorescence of phosphorescence data reported for carbaryl in a number of solvents.</td>
<td>71</td>
</tr>
<tr>
<td>2.4</td>
<td>Fluorescence (singlet-state) lifetimes of carbaryl and 1-naphthol measured by TCSPC in buffered aqueous solutions.</td>
<td>72</td>
</tr>
<tr>
<td>2.5</td>
<td>Predicted [HO-]ss for water samples taken from Old Woman Creek (OWC) in June, August, and September of 1998 in the pH adjusted water.</td>
<td>73</td>
</tr>
<tr>
<td>3.1</td>
<td>Water quality characteristics and measured rate coefficients for alachlor degradation in the natural water samples.</td>
<td>191</td>
</tr>
<tr>
<td>3.3</td>
<td>Water quality characteristics and measured rate coefficients for alachlor degradation in the natural organic matter isolate (XAD-8 extract) of Old Woman Creek.</td>
<td>193</td>
</tr>
</tbody>
</table>
3.4 Predicted hydroxyl radical production from H2O2 in selected water samples and isolates compared to the measured production (White, 2000) ... 194

3.5 Effect of pH on the rate coefficient of alachlor transformation in selected NOM isolates and proton saturated OWC 9-14-99 RR .............................................................. 195

3.6 Reported properties for NOM isolate samples used in this study ...................... 196

3.7 Effect of iron amendments on alachlor degradation in SRFA and OWC 9-14-99 RR water .............................................................................................................. 197

3.8 Iron speciation (calculated as % of total) in water samples used for the iron amendment experiments. Binding of iron by NOM was not considered ................... 198

3.9 Effect of iron level on the photoinduced degradation of alachlor ....................... 199
LIST OF FIGURES

Figure

1.1 Direct and indirect photolytic processes occurring in natural waters (adapted from Hoigné, 1990) ................................................................. 18

2.1 Map of Old Woman Creek Estuarine Reserve (OWC), Huron, OH. Water samples were obtained from the Inlet (IN), Railroad (RR), and Outlet (OUT). .................................................................................. 74

2.2 Spatial and temporal variability in the molar absorptivity (e) at λ = 280 nm (A), nitrate concentration (B), and total iron level (C) measured in the OWC wetland water samples during the 1998 field season............................................. 75

2.3 Variation of screening factor with wavelength for wetland water samples. .......... 76

2.4 Photoinduced degradation of carbaryl in OWC wetland water samples at their natural pH (~8). Error bars represent the 95% CI. ......................................................... 76

2.5 Photoinduced degradation of carbaryl in pH adjusted (~4) water samples. Error bars represent the 95% CI. .................................................................................. 77

2.6 Photoinduced degradation of carbaryl in OWC water sampled from the Inlet site on June 29, 1998 at ambient pH (~8). ................................................................. 77

2.7 Photoinduced degradation of carbaryl in the OWC 6-29-98 Inlet water in pH adjusted (4.37) water samples. ................................................................. 78
2.8 A comparison of the corrected (for dark reaction) rate coefficients for the photoinduced degradation of carbaryl in altered (pH 4) and unaltered (pH 8) OWC samples. Error bars represent the propagated error (one standard deviation). 78

2.9 Base-catalyzed elimination pathway for the N-methyl carbamate, carbaryl. 79

2.10 Carbaryl UV/VIS absorption spectra as a function of pH. 80

2.11 Change in UV/VIS absorption spectrum of carbaryl (pH = 9.04) with time. 80

2.12 Dependency of the direct photolysis rate coefficient, $k_{obs}$ (hr$^{-1}$), for carbaryl degradation on the pH ([OH$^{-}$]). Dotted lines represent the 95% CI. 81

2.13 Dependency of correct (for dark reaction) rate coefficient and quantum yield for the direct photolysis of carbaryl at $I = 366$ nm. Dotted lines represent the 95% CI. 81

2.14 Effect of 1-naphthol on the photoinduced degradation of carbaryl. 1-Naphthol added at the various mole ratios given in the legend. 82

2.15 Fluorescence lifetime measurements for carbaryl using TCSPC. 83

2.16 Fluorescence lifetime measurements for 1-naphthol using TCSPC. 83

2.17 Direct photolysis of carbaryl in high pH (8.00) solutions with and without argon sparging. 84

2.18 The contribution that direct and indirect photolysis have to $k_{corrected}$ for carbaryl degradation in tested wetland waters. Error bars represent the propagated error (one standard deviation). 85
2.19 The contribution that direct and indirect photolysis have to kcorrected for
carbaryl degradation in the pH adjusted waters. Error bars represent the
propagated error (one standard deviation)................................. 85

2.20 Multiple regression analysis of kobs (min⁻¹) for carbaryl photodegradation
versus the [DOC] (mg-C/L) and [Nitrate] (M)................................. 86

2.21 Correlation between nitrate level with pseudo-first order rate coefficient
(corrected for the dark reaction and normalized to the TOC) for the
samples run in pH adjusted (~4) OWC wetland water and control solutions .... 87

2.22 Correspondence of nitrate level to the corrected (for the dark reaction) rate
coefficient for carbaryl degradation. Plot shows the spatial and temporal
trends of nitrate levels. Error bars represent the propagated error (95%
CI)....................................................................................... 88

2.23 Positive correlation observed between the nitrate level and the rate
coefficient (kcorrected; corrected for the dark reaction) measured for the
photodegradation (at λ = 366 nm) of carbaryl. Each kcorrect was
normalized to the screening factor determined for a given OWC water
sample to correct for differences due to inner filter effects. Error bars
represent the propagated error (one standard deviation)..................... 89

2.24 Inverse correlations observed between NOM (measured as the TOC) and
alkalinity (inset) and the rate coefficient (kcorrected; corrected for the dark
reaction) measured for the photodegradation (at λ = 366 nm) of carbaryl.
Each kcorrect was normalized to the screening factor determined for a
given OWC water sample to correct for differences due to inner filter
effects. Error bars represent the propagated error (one standard deviation)..... 89

2.25 Comparison of corrected (for the dark reaction) rate coefficients
determined for the photoinduced degradation of carbaryl in low nitrate (<
50 mM) OWC samples. Hydrophobic and hydrophilic samples were
obtained by dissolving XAD-8 and -4 isolates in buffered MilliQ water.
Error bars represent the propagated error (95% CI).............................. 90
2.26 UV/VIS spectra providing evidence that carbaryl does not form charge transfer complexes with the NOM to a significant extent.................................................... 91

2.27 Relationship between the light screening factor measured at \( I = 290 \) nm and corrected (for the dark reaction) rate coefficients for carbaryl degradation at pHs of 8 (A) and 4 (B).................................................................. 92

3.1 Proposed scheme for the direct photolysis of alachlor (adapted from Schmidt, et al., 1995 and Penuela and Barcelo, 1996).......................................................... 200

3.2 Map of Old Woman Creek Estuarine Reserve (OWC), Huron, OH. Water samples were obtained from the Inlet (IN), Railroad (RR), and Outlet (OUT).................................................................. 201

3.3 Peroxidase-catalyzed oxidation of Leuco Malachite Green by hydrogen peroxide (Zepp et al., 1988). ................................................................. 201

3.4 Comparison of the measured photoinduced degradation of alachlor in Old Woman Creek water samples at the natural pH (~8) and pH adjusted samples. ................................................................. 202

3.5 Comparison of the photoinduced degradation of alachlor in various engineered wetlands located in agricultural watersheds. Data from two pHs are presented. Error bars represent the 95% CI determined from least squares analysis of the data. ................................................................. 203

3.6 Molar absorptivities (M\(^{-1}\)cm\(^{-1}\)) of modified samples of the OWC 9-14-99 RR raw water................................................................. 204

3.7 Observed pseudo-first order rate coefficient determined from experiments conducted with modified samples of the OWC 9-14-99 RR wetland water sample................................................................. 204
3.8 Correlation between the DOC level measured in the wetland water samples and the factor that alachlor degradation was promoted at the lower pH. The Champaign Co. water was not included in this plot................................. 205

3.9 Correlations of kobs (hr-1) and the TOC level in wetland water samples at high (a) and low (b) pH. Error bars represent the 95% CI of determined rate coefficients. Note that the data from the OWC 6-29-98 IN samples were not included on these plots. Outliers in plot (a) were the Fulton Co. and the OWC 9-14-99 RR waters. ................................................................. 206

3.10 Plots of kobs (hr-1) versus the molar absorptivity at 320 nm and 280 nm at the high (a) and low (b) pH wetland water samples. MilliQ water controls are also included in the plots. The rate constant for the OWC 6-29-98 IN water was corrected for the nitrate contribution (0.0978 hr-1). ................................. 207

3.11 Timecourses presented comparing the photodegradation of alachlor in OWC XAD-8 isolate at high and low pH to natural waters of similar composition. ........................................................................................................ 208

3.12 Plot of total iron (FeTotal) measured in the wetland water samples versus the factor that the reactions were promoted upon lowering the pH of the samples. ........................................................................................................ 209

3.13 Correlation between Fe(ppb):TOC (mgC/L) ratio to observed rate coefficient for alachlor degradation................................................................. 209

3.14 Relationship of OWC XAD-8 TOC (mgC/L) to kobs (hr-1) for alachlor photodegradation. Data presented are for the uncorrected (black) and corrected (white) for inner filter effects values of kobs. Line indicates model fit. ........................................................................................................ 210

3.15 Correlation between TOC and kobs (normalized to the TOC and corrected for light screening effects) for alachlor degradation promoted by the OWC XAD-8. ........................................................................................................ 210
3.16 The levels of H2O2 measured in several of the OWC water samples during timecourses.

3.17 Rate coefficients measured for alachlor degradation (kobs) (left axis) and iron levels measured (right axis) plotted against the pH for selected NOM isolates and the proton saturated OWC 9-14-99 RR wetland water sample.

3.18 Plot of normalized (to the TOC) rate coefficient measured for alachlor degradation versus the pH for selected NOM isolates and proton saturated OWC 9-14-99 RR wetland water sample.

3.19 Plot of the normalized (to the TOC and Fe) rate coefficient measured for alachlor degradation versus the pH. Error bars are the calculated propagated error for the normalization calculation based upon the standard deviations of all measured values.

3.20 The effect that addition ~2 mM Fe to SRFA solutions had on kobs for the photoinduced degradation of alachlor.

3.21 The effect that addition of ~2 mM Fe to OWC 9-14-99 RR water samples had on the normalized (to [TOC]) kobs for the photoinduced degradation of alachlor.

3.22 Photoinduced degradation of alachlor in SRFA and LFFA solutions. Results are compared with those obtained from irradiation of alachlor in buffered MilliQ water and NOM solutions that had been spiked with either or both methanol (0.05 M; MeOH; light gray bars) and iron (~25 ppb Fe; black bars).

3.23 Effect of FeTotal (ppb) on the measured rate coefficient for the photoinduced degradation of alachlor in selected NOM isolate solutions (pH = 3.60).
3.24 Molar absorptivities (M-1cm-1) calculated for the SRFA and LFFA solutions as a function of wavelength. For comparison, the molar absorptivity of the Suwannee River raw water is also shown................................. 218

3.25 Extrapolation of kobs for alachlor degradation from linear portion of NOM vs FeTotal plots. (a) SRFA and (b) LFFA.................................................................................. 219

3.26 Comparison of kpred and kobs for the iron promoted degradation of alachlor in reconstituted SRFA (a) and LFFA (b).................................................................. 220

4.1 Validation of the computer code............................................................. 261

4.2 Variation of the slope ("S") of the absorption coefficient as a function of irradiation time for altered OWC RR 9-14-99 water. ................................................. 262

4.3 Pseudo-first order rate coefficients (decrease of absorption coefficients (m-1) with irradiation time) measured for the photobleaching of Old Woman Creek Water sampled from the railroad site on 9-14-99 in the wavelength range from 290 to 450 nm.................. 262

4.4 Variation of “S” as a function of irradiation time for solutions with various concentrations (mgC/L) of OWC XAD-8 NOM isolate................................. 263

4.5 Wavelength variation of kOBS for photobleaching of OWC XAD-8 isolate solutions................................................................. 263

4.6 Variation of calculated “S” as a function of irradiation time observed for the OWC XAD-8 sample at high (7.12) and low (4.08) pH................................. 264

4.7 Wavelength variation of the kOBS for photobleaching for OWC XAD-8 sample at high (7.12) and low (4.08) pH................................................................. 264

4.8 Variation of calculated “S” as a function of irradiation time observed for the OWC RR 9-14-99 H+ water measured at several pHs................................. 265
4.9 Wavelength variation of the kOBS for photobleaching for the OWC 9-14-99 RR H+ water sample at several pHs.

4.10 Variation of calculated “S” as a function of time observed for the Fulton Co. UF isolate solutions measured at several pHs. The lower curve shows the results when a pH 4 solution is sparged with argon.

4.11 Variation of the photobleaching kOBS for Fulton Co. UF in the wavelength range 290-450 nm. The lower curve represents photobleaching rate when a pH 4.08 solution is argon sparged. The inset shows the fraction of photobleaching reduction achieved for all wavelengths in the test range (290-450 nm).

4.12 Variation of calculated “S” as a function of irradiation time observed for SRFA solutions measured at several pHs.

4.13 Wavelength variation of the photobleaching kOBS (hr-1) for SRFA solutions at several pHs.

4.14 Change in the calculated “S” during irradiation for SRFA solutions containing various amounts of iron.

4.15 Change in the calculated “S” during irradiation for LFFA solutions containing various amounts of iron.

4.16 Change in photobleaching kOBS for SRFA solutions containing various amounts of iron.

4.17 Change in photobleaching kOBS for LFFA solutions containing various amounts of iron.

4.18 Drop in absorbance observed at the 2-hour time point using data from the OWC RR 9-14-99 proton saturated water sample as an example.
4.19 Relationship between measured DOC (mgC/L) and photobleaching for OWC XAD-8 solutions ................................................................. 273

4.20 Relationship between photobleaching rate coefficient at several wavelengths and the observed rate coefficient (kobs) for alachlor degradation measured in an OWC XAD-8 solution (pH 4.08) .................................................. 274

4.21 Relationship between photobleaching rate coefficient at several wavelengths and the pH (A), total iron (B), and the observed rate coefficient (kobs) for alachlor degradation (C) measured in SRFA solution .................................................................................. 275

4.22 Relationship between photobleaching rate coefficient at several wavelengths and the pH (A), total iron (B), and the observed rate coefficient (kobs) for alachlor degradation (C) measured in OWC RR 9-14-99 H+ water samples ................................................................................................. 276

4.23 Relationship between photobleaching rate coefficient at several wavelengths and the pH (A), total iron (B), and the observed rate coefficient (kobs) for alachlor degradation (C) measured in Fulton Co. UF isolate. ............................................................................................................. 277

4.26 Relationship between photobleaching rate coefficient at several wavelengths and the observed rate coefficient (kobs) for alachlor degradation measured in SRFA solutions of varying iron concentrations (pH = 3.6). Data presented for select wavelengths ................................................................. 279

A.1 UV/VIS for OWC water samples collected on 6-29-98 .............................................. 304

A.2 UV/VIS for OWC water samples collected on 9-14-99 .............................................. 305

A.3 UV/VIS for OWC Inlet 6-29-98 at high (~8) and low (~4) pH ................................. 305

A.4 UV/VIS for OWC RR 6-29-98 at high (~8) and low (~4) pH ..................................... 306
A.5 UV/VIS for OWC OUT 6-29-98 at high (~8) and low (~4) pH..........................306
A.6 UV/VIS for OWC AUG RR at high (~8) and low (~4) pH. .............................307
A.7 UV/VIS for OWC IN 9-8-98 at high (~8) and low (~4) pH............................307
A.8 UV/VIS for OWC RR 9-8-98 at high (~8) and low (~4) pH.............................308
A.9 UV/VIS for OWC OUT 9-8-98 at high (~8) and low (~4) pH..........................308
A.10 UV/VIS for pH adjusted and proton saturated OWC IN 6-29-98 sample...........309
A.11 Photoinduced degradation of carbaryl in OWC IN 6-29-98 water sample........310
A.12 Photoinduced degradation of carbaryl in OWC RR 6-29-98 water sample........310
A.13 Photoinduced degradation of carbaryl in OWC OUT 6-29-98 water sample........311
A.14 Photoinduced degradation of carbaryl in OWC RR 8-24-98 water sample........311
A.15 Photoinduced degradation of carbaryl in OWC IN 9-8-98 water sample..........312
A.16 Photoinduced degradation of carbaryl in OWC RR 9-8-98 water sample..........312
A.17 Photoinduced degradation of carbaryl in OWC OUT 9-8-98 water sample........313
A.18 Photoinduced degradation of carbaryl in pH 8.00 borate buffer (10mM).........313
A.19 Photoinduced degradation of carbaryl in pH 7.98 carbonate buffer (2 mM).....314
A.20 Photoinduced degradation of carbaryl in OWC IN 6-29-98 pH adjusted water sample................................................................................................... 314

A.21 Photoinduced degradation of carbaryl in OWC RR 6-29-98 pH adjusted water sample................................................................................................... 315

A.22 Photoinduced degradation of carbaryl in OWC OUT 6-29-98 pH adjusted water sample................................................................................................... 315

A.23 Photoinduced degradation of carbaryl in OWC IN 6-29-98 pH adjusted water sample that was proton saturated............................................................... 316

A.24 Photoinduced degradation of carbaryl in OWC RR 8-24-98 pH adjusted water sample................................................................................................... 316

A.25 Photoinduced degradation of carbaryl in OWC RR 8-24-98 pH adjusted water sample with nitrate (1 mM) spike............................................................. 317

A.26 Photoinduced degradation of carbaryl in OWC IN 9-8-98 pH adjusted water sample................................................................................................... 317

A.27 Photoinduced degradation of carbaryl in OWC RR 9-8-98 pH adjusted water sample................................................................................................... 318

A.28 Photoinduced degradation of carbaryl in OWC OUT 9-8-98 pH adjusted water sample................................................................................................... 318

A.29 Photoinduced degradation of carbaryl in pH 4.35 phosphate buffer (5 mM)..................................................................................................................... 319

A.30 Photoinduced degradation of carbaryl in pH 4.35 buffered XAD-8 solution............................................................................................................... 319
A.31 Photoinduced degradation of carbaryl in pH 4.35 buffered XAD-4 solution

B.1 UV/VIS for OWC 6-29-98 Inlet water at low and high pH

B.2 UV/VIS for OWC 9-14-99 Railroad water at low and high pH

B.3 UV/VIS of OWC 9-8-98 Outlet water

B.4 UV/VIS of Suwannee River water (diluted to 5.95 mgC/L)

B.5 UV/VIS of Defiance County wetland water sample at low and high pH

B.6 UV/VIS of Fulton County wetland water sample

B.7 UV/VIS spectra of Van Wert County wetland water at low and high pH

B.8 UV/VIS spectra of Champaign County wetland water at low and high

B.9 Photodegradation of Alachlor in buffered MilliQ water samples at pH 8.08 (a) and 4.21 (b)

B.10 Photoinduced degradation of alachlor in OWC 6-29-98 Inlet water at the natural pH (a) and pH =2.78 (b)

B.11 Photoinduced Degradation of alachlor in OWC 9-14-99 Railroad water at the natural pH (a) and a pH of 4.08 (b). An experiment performed in argon sparged solution is also presented (b)

B.12 Photoinduced degradation of alachlor in OWC 9-8-98 Outlet water at the natural pH (8.09) of the water
B.13 Photoinduced degradation of alachlor in the Defiance Co. wetland water.
(a) unadjusted pH and (b) pH adjusted water..................................................... 330

B.14 Photoinduced degradation of alachlor in the Fulton Co. wetland water.
(a) unadjusted pH and (b) pH adjusted water..................................................... 331

B.15 Photoinduced degradation of alachlor in the VanWert Co. wetland water.
(a) unadjusted pH and (b) pH adjusted water..................................................... 332

B.16 Photoinduced degradation of alachlor in the Champaign Co. wetland
water. (a) unadjusted pH and (b) pH adjusted water......................................... 333

B.17 Photoinduced degradation of alachlor in Suwannee River raw water (pH =
4.26)................................................................................................................... 334
CHAPTER 1

INTRODUCTION

1.1 Nature and Scope of the Research

Non-point source (NPS) pollution threatens the quality of natural waters globally. The U.S. EPA states that non-point source pollution is "the leading cause of surface and groundwater quality impairment" (1996). Several pieces of legislation in the past decade have been written and enacted to protect natural waters from non-point source pollution including the Section 319, Management of Non-point source pollutants (EPA) of the Clean Water Act (CWA) and Section 6217 of the Coastal Zone Act Reauthorization Amendments of 1990 (CZARA Program; EPA/NOAA). Recently, the U.S. EPA has proposed a strategy for strengthening the management of non-point source pollution. In the fiscal year of 2001, Congress appropriated $238 million for the continued support of States, Territories, and Tribes in implementing Section 319. It is clear from this level of support that the issue of non-point source pollution is of critical importance (U.S.EPA, 2001). Non-point source pollution from surface runoff contaminated with agrochemicals threatens communities that rely on surface water for their drinking water supply and recreation. Four times more waters were reported to be polluted from agricultural
chemical runoff than from municipal sources (U.S. EPA, 1992). Non-point source pollution from agricultural contaminants is especially important in watersheds where the dominant land use is row crop agriculture (Baker, 1993). A long-term study that monitored agrochemical concentrations in seven Lake Erie tributaries in Ohio from 1983-1991 indicated that monthly average concentrations of atrazine and alachlor generally exceeded maximum contaminant levels (MCLs) for at least one month following herbicide application (Richards and Baker, 1993).

Non-point source contamination is difficult to control because it may be distributed across large areas of a watershed. Thus, the scope of this problem calls for a watershed approach when dealing with the problem. Wetlands may provide a means of managing water quality since the hydrology of a watershed will often result in the collection of water from diffuse sources into wetland basins before final discharge to receiving waters. Many researchers have noted an improvement in the quality of water as it passes through a wetland and have attributed the improvement to a combination of physical and chemical factors. Because of this research, interest has increased in preserving and restoring coastal wetlands and riparian zones, and engineering new wetland areas for the management and improvement of surface water quality.

Wetlands are characterized by their biological activity, hydrologic properties, and their sediments. These features work together to improve water quality. The presence of vegetation can slow the flow of runoff and prevent erosion by dissipating hydrologic energy. Vegetation and algae can also absorb excess nutrients from runoff thereby reducing nutrient load on final receiving waters. Furthermore, the biological processes
that utilize these nutrients result in the manufacturing of carbon in the form of biological material. This material will eventually settle and undergo decay, thus, inducing microbial activity, particularly in the sediments. Decay processes can lead to the development of anoxic sediments where excess nitrate can be reduced and lead to denitrification.

Sediments can also provide a storage compartment for organic or heavy metals and precipitates that drop out of solution because of the reduced flow (and carrying capacity) through wetlands. Overall, these characteristics facilitate the storage and transformation of commonly studied NPS contaminants.

An active research area is modeling the loss of NPS pollution through wetlands. One way to model these systems is to use plug-flow (unidirectional) reactor kinetics such as:

\[ P_i Q - Q \left( P_i + \frac{\partial P_i}{\partial x} dx \right) + r_p dV = \frac{\partial P_i}{\partial t} dV \]  

(1.1)

where

\[ r_p = \frac{dP_i}{dt} = -k_{ab} [P] \]  

(1.2)

where \( P_i \) represents the pollutant mass concentration in the inflow, \( Q \) is equal to the flow rate; \( \frac{\partial P_i}{\partial t} dV \) is the rate of accumulation of \( P_i \) in the system, and \( r_p \) is the rate of transformation of \( P_i \) in the system (Weber and DiGiano, 1996). Because of the complexity of the processes occurring in wetlands, this model serves as a framework for viewing how these processes could be modeled. The term, \( r_p \), sums the effect of a process that leads to a loss of a particular NPS contaminant as the water passes through
Examples of numerous processes that could be modeled this way would include: 

(1) Volatilization;
(2) Vegetative Uptake (nutrients and heavy metals research);
(3) Partition (and re-release) into sediments; and
(4) Algal and Microbial transformation and uptake of nutrients

Rodgers and Dunn (1992) developed a non-rigorous model to guide engineers in the design of constructed wetlands for pesticide removal along similar lines. Pesticide fate was modeled according to first-order kinetics where the overall rate constant for pesticide loss was defined as the sum of the individual rate coefficients for the various processes contributing to either the transfer or transformation of a pesticide (i.e., sorption, solubility, flow, infiltration, retention, volatilization, photolysis, hydrolysis, and biotransformation). The model relates the transformation and transfer rate of a pesticide to the ability of a particular wetland to reduce NPS pollutants and ultimately, can be used to predict the residence time required to achieve a desired removal. Conceptually, this model provides some useful ideas for predicting the fate of NPS contaminants in wetlands, but is limited because the rates of many transformations occurring in wetlands are unknown. The model, at best, becomes empirical where only a “bulk” overall constant can be measured. Currently, EPA has developed the Exposure Analysis Modeling System (EXAMS) as a tool to predict the fate of pesticides in aquatic systems (Armbrust, 2000). This model utilizes reported rate coefficients for the transformation or transfer of NPS
contaminants. Overall, there is a growing need for reliable and accurate environmental fate data.

One transformation process that has received little attention in its contribution to overall pollutant fate in wetlands is the role of photochemical reactions. As a first attempt to evaluate the relative importance of a particular transformation processes, my research will examine and evaluate the photolytic contribution to NPS pollutant transformation in wetlands surface waters. The examination of wetland water constituents that facilitate the degradation of specific target NPS contaminants is examined in Chapters 2 and 3. In Chapter 4, I investigate the influence of photochemical reactions on dissolved natural organic matter (NOM), which is suspected to play a key role in mediating NPS contaminant degradation.

1.2 Photochemistry in Natural Waters

Photochemical processes in natural waters are initiated by when a particular constituent (molecule A) absorbs a photon (Figure 1.1). The ability of a molecule to absorb light is related to molecular substructures called chromophores and include functional groups such as alkenes, carbonyls, aromatic and heterocycles, nitro, etc.. A UV/VIS absorption spectrum measures the probability for absorption. The probability is quantified by the extinction coefficient (\( e \)). A high extinction at a given wavelength (large absorption band) means the absorption is very likely.
A molecule that absorbs a photon is said to be in its singlet state (\(^1\text{A}\)). There are number of primary pathways \(^1\text{A}\) can take to dissipate its energy from the electronic excitation. Some of these pathways do not result in chemical transformation because \(^1\text{A}\) releases its energy to return to its ground state through unproductive processes such as internal conversion (thermal release) and fluorescence (emission of light). Alternatively, photons may provide enough energy to effect chemical transformation such as homolytic bond cleavage or the ejection of an electron (\(e^-\)). When absorption of light results in a chemical transform it is called direct photolysis. Although \(^1\text{A}\) is a relatively unstable, it may have a long enough lifetime to permit reaction. The interaction of \(\text{O}_2\) with singlet states is well known and it enhances \(^1\text{A}\) conversion to its excited triple state, \(^3\text{A}\). Intersystem crossing of \(^1\text{A}\) to \(^3\text{A}\), although spin-forbidden, is rather common. \(^3\text{A}\) is a relatively more stable excited state than \(^1\text{A}\) because of the difficulty the molecule has in relaxing to its ground state due to the unpaired spins of its electrons. The lifetimes are significantly long enough to allow \(^3\text{A}\) to react with a number of substrates.

Reactions of \(^1\text{A}\) or \(^3\text{A}\) with various substrates can produce a number of reactive species, X (Figure 1.1). The relative efficiency of this indirect photolytic process is quantified by determining the ratio (\(\Phi\)) of the number of molecules formed by a particular chemical reaction to the total number of photons absorbed by \(\text{A}\). The rate of a primary process can be quantified by the term \(k_{\text{A,i}}[\text{A}]\Phi_i\), which mathematically states that the rate of transformation of \(\text{A}\) by reaction "i" is the product of the specific light absorption rate constant (which is a function of the light intensity and molar extinction coefficient of \(\text{A}\)), concentration of \(\text{A}\), and the quantum yield for the formation of X.
In natural waters, photochemical reactions occur mostly in the upper water column (so called photic zone). The extent of the photic zone will depend on how strongly water constituents absorb sunlight (i.e., their attenuation). NOM contains numerous chromophores with known photolytic properties (certain transition metal complexes, amino acids, flavinoid, carotenoids, carbonyls, etc.) (Zafiriou et al., 1984; Larson et al., 1992; Tatsumi et al., 1992; Faust et al., 1993) as well as numerous unidentified chromophores. When NOM absorbs a photon of light, the excited singlet (\(^1\)NOM) is too short lived for significant reaction. However, the singlet may undergo intersystem crossing to a triplet state (\(^3\)NOM), which has a significantly longer lifetime (Figure 1.1). Quantum yields (\(\Phi_{\text{isc}}\)) for intersystem crossing to the triplet state, measured by time-resolved photoacoustic spectroscopy, range from 0.91 to 0.35 (pH range from 2 to 9.5) from Armadale fulvic acid, making it the dominant photophysical process involving NOM in this system (Brucoleri et al., 1993). Other processes by which excited NOM can dissipate energy (combined \(\phi\) generally < 0.22) include the ejection of electrons to yield solvated electrons (e\(^-\)aq), homolytic cleavage of chemical bonds or hydrogen abstraction to form carbon-centered radicals (R\(^*\)), and fluorescence (Figure 1.1). While much of the \(^3\)NOM decays to ground state by the non-productive pathways, a fraction may undergo energy transfer to neighboring molecules. Substances capable of quenching triplet excited state molecules include O\(_2\) (by far the most common quencher), NOM itself, and solutes. The latter two appear to be more important in anoxic waters. Energy transfer (or other reactions involving e\(^-\)aq and R\(^*\)) to O\(_2\) generates activated oxygen species such as singlet oxygen (\(^1\)O\(_2\)), hydroxyl radicals (HO\(^*\)), hydrogen peroxide (H\(_2\)O\(_2\)),
hydroperoxyl radical and superoxide (HO$_2^*$/O$_2^*$), and organic peroxyl radicals (ROO*) (Cooper et al., 1989; Hoigné et al., 1990; Haag et al., 1990; Miller, 1994). It is also possible for solutes to react with excited state NOM resulting in energy transfer (Zepp et al., 1985) or electron transfer (Canonica et al., 1995; Canonica et al., 2001) reactions.

The photochemistry of natural waters is further complicated by the chemistry of reactive intermediates. For example, superoxide can react with hydronium ions to form H$_2$O$_2$. In the presence of trace metals (Fe(II), Cu(I)), H$_2$O$_2$ can produce HO$^*$ through the Fenton reaction (Cooper et al., 1983; Faust et al., 1993). Likewise, carbon-centered radicals can react with O$_2$ to form organoperoxyl radicals, ROO$^*$ (Faust et al., 1987; Brucoleri et al., 1993). HO$^*$ can react with inorganic anions to form corresponding radicals (e.g., Br$^-$ or CO$_3^{2-}$) (Larson and Zepp, 1988). The result of these processes is a steady-state radical flux that can influence the fate of solutes in sunlit natural waters (Blough and Zepp, 1996). The types of reactive species formed are dependent upon the composition of the photosensitizer and the chemistry of the natural water. Steady-state concentrations of reactive species are usually directly proportional to the NOM concentration, up to a point: the limit is reached when NOM reaches a level that self-quenching outcompetes other photochemical processes. (Cooper et al., 1983; Haag et al., 1986).

Photoreactive non-NOM water constituents may influence NOM photochemistry by working to transform NOM through indirect processes. Nitrate is capable of producing hydroxyl radicals (HO$^*$) with quantum yields ranging from 9.2-17 $\times 10^{-3}$ when
irradiated at wavelengths greater than 290 nm (Mabury and Crosby, 1994). Nitrite, a photolysis product of nitrate, can also produce HO· at quantum yields ranging from 0.015 to 0.08 between 298 and 371 nm, respectively (Zafiriou and Bonneau, 1987). In aqueous systems that receive agricultural runoff, the nitrates may be sufficiently high to produce high steady-state concentrations of HO·. Indeed, calculations (noonday sunlight at 40° latitude) based upon nitrate levels measured in a wetland that drains an agricultural watershed (Chapter 2.3 of this work) predicted HO· concentrations that were an order of magnitude higher than that reported for other water bodies (~10^{-18}-10^{-16} M)(Zepp et al., 1987). Although the amount of nitrates present in aquatic systems depend on the load and internal cycling by biota, it could be high enough in some system to impact the NOM.

1.3 Relationship of NOM Photochemistry to Contaminant Fate in Wetlands

Several studies have provided evidence that photochemical processes may mediate contaminant transformation in natural waters (Armbrust, 2000; Canonica et al., 1995; Chiron et al., 1995; Hoigné, 1990; Minero, et al., 1992; Kolpin and Kalkhoff, 1993; Faust and Zepp, 1993; Frimmel and Hessler, 1994; Simmons and Zepp, 1986; Zepp et al., 1987; Mabury and Crosby, 1994; Wilson and Mabury, 2000; Torrents et al., 1997; Brezonik and Fulkerson-Brekken, 1998). Field studies conducted in streams and rivers located in Iowa have shown that an increase in the number of sunlight hours (from winter to summer) results in a significant increase in the overall transformation coefficient (by as much as a factor of four) for atrazine (Kolpin and Kahlkoff, 1993). Geyer et al. (1996)
demonstrated that the photolytic degradation of rice field pesticides was significant due to the concentration of contaminants in surface microlayers. Several studies have also investigated the effect that nitrate can have in influencing contaminant fate through photochemical processes (Zepp et al., 1987; Mabury and Crosby, 1994; Mabury et al., 1999; Torrents et al., 1997). Thus, sunlight enhanced transformation processes may be an important degradation pathway for organic pollutants associated with agricultural runoff and other non-point sources in surface waters.

In wetland surface waters, sunlight induced reactions have significantly contributed to the chemical transformation of agricultural pollutants through several possible indirect and direct photolytic pathways (see Hoigné, 1990 for a review). Several physical characteristics of wetlands indicate they could be efficient photochemical reactors. Wetlands generally have large surface areas and shallow depths that would allow significant sunlight exposure and penetration throughout the water column. Moreover, wetlands are rich in natural dissolved organic matter (NOM) which is capable of absorbing sunlight and catalyzing the phototransformation of organic compounds by indirect pathways. As a result, wetlands are capable of acting as giant "photoreactors" that may facilitate the degradation of non-point source pollutants.

As a photoreactor, wetlands may provide an important medium for commonly used agricultural chemicals to undergo direct phototransformation. This process occurs when light is absorbed by a contaminant and leads to subsequent degradation (Figure 1.1) (Kolpin and Kalkhoff, 1993; Woodburn et al., 1993). Partially degraded pollutants may also undergo photolysis reactions (Simmons and Zepp, 1986; Hwang et al., 1987).
Additionally, natural wetland constituents may aid in the indirect photodegradation of contaminants. Many wetlands are eutrophic and receive copious amounts of organic matter from both autochthonous and allochthonous sources in comparison to other water bodies (lakes and rivers). Much of the NOM in natural waters are comprised of decomposed organic matter and/or extracellular products as well as amorphous humic substances which contain a variety of chromophoric functional groups that absorb sunlight. Because of their high NOM content and stronger absorption of sunlight, wetlands waters have been reported to have greater near-surface photoreactivity than other natural waters (Valentine and Zepp, 1993).

Recent evidence suggests that indirect photolysis mediated by NOM of organic pollutants may be very important in some natural water systems (Canonica et al., 1995; Chiron et al., 1995; Hoigné, 1990; Minero, et al., 1992; Kolpin and Kalkhoff, 1993; Faust and Zepp, 1993; Frimmel and Hessler, 1994; Simmons and Zepp, 1986). For many pesticides and herbicides present in agricultural runoff, direct photolysis is a less important pathway because these contaminants do not readily absorb photons at wavelengths present in sunlight. Studies have shown that the presence of humic substances enhanced the photolysis of numerous organic compounds and herbicides (Simmons and Zepp, 1986: Minero et al., 1992; Chiron et al., 1995) and in some cases, the effect was attributed to the direct reaction of the target compound with photochemically generated excited states of NOM and uncharacterized photooxidants derived from the NOM (Canonica et al., 1995).
The presence of non-NOM wetland water constituents can also affect the production of reactive intermediates that degrade contaminants. In natural waters, a principal source of HO*, a powerful and unselective oxidant, is nitrate photolysis (Hoigné et al., 1989; 1990). Deliberate addition of nitrate to solutions containing selected environmental contaminants increased their photolysis rates (Kotzias et al., 1982; Torrents et al., 1997), and the effect was ascribed to the reaction of target contaminants with the HO* generated from nitrate photolysis. In addition, iron can participate in primary (photolysis of iron hydroxy complexes) (Faust and Hoigné, 1990) and secondary photolytic pathways (Fenton chemistry) to produce HO* (Voelker et al., 1997). If such HO* precursor compounds are present in high enough concentrations compared to scavenger concentrations, then HO* may be able to attain steady-state concentrations high enough to affect the fate of contaminants.

The efficiency of these photolytic reactions are highly variable. Although photosensitization by NOM is the major source of environmental photooxidants, it is also a major sink for many of the same species, resulting in very low steady-state concentrations in natural surface waters (Faust and Hoigné, 1987). The presence of NOM has also been shown to inhibit the photodegradation rate of contaminants, and the effect was attributed to the quenching of excited states and the scavenging of reactive intermediates and photons (Woodburn et al., 1993; Miller et al., 1980; Hwang et al., 1987; Larson and Zepp, 1988). Despite this effect, increased NOM concentration generally results in increased indirect photolysis rates (Cannonica et al., 1995a).
Furthermore, particulate organic matter was found to enhance photolysis rates due to light scattering increasing the diffuseness of light in suspensions (Miller and Zepp, 1979). Ultimately, the photoinduced degradation of a NPS contaminant in a particular natural water system will depend on several factors including: the amount of NPS contaminant and NOM present, the light absorbing characteristics of each species, the type of reactive intermediates the NOM is able to generate, the presence of other reactive photochemical reactants such as metal complexes (Sulzberger et al., 1994) and nitrates (Mabury and Crosby, 1994), turbidity, basin mixing, and vegetative cover. These factors influence transformation rates through their effect on photon flux on the basin and participation in competitive processes that may or may not aid in the destruction of pollutants. Nitrate, as a precursor in photoinduced hydroxyl radical production (Mabury and Crosby, 1994; Haag and Hoigné, 1985), is of particular concern in natural waters because nitrate levels in agricultural runoff coincide with the pesticide pulse during spring flush (Zepp et al., 1987).

The kinetics of indirect photolysis have been described by several authors (Leifer, 1988; Tratnyek et al., 1991; Garcia, 1994; Tratnyek et al., 1994; Canonica et al., 1995; Hoigné, 1990; Haag, 1988). Certain organic compounds have been identified that only react with specific reactive intermediates (Hoigné, 1990; Blough and Zepp, 1995). These compounds act as "molecular probes" [P] to help identify the types and quantify the amount of reactive species generated from the irradiation of a natural water (Faust et al., 1987; Tratnyek et al. 1994; Tratnyek and Hoigne, 1994). Steady-state concentrations of
the reactive species, \([\text{transient}]_{\text{tr}}\), can be calculated from the rate of probe disappearance in a well-mixed system according to:

\[
-\frac{d[P]}{dt} = k_p[P][\text{transient}]_{\text{tr}} = k_{\text{obs}}[P] \tag{1.3}
\]

where \([P]\) is the concentration of the probe and \(k_p\) is the reported rate constant of the probe with reactive transient species of interest. This equation applies for reactions in an optically thin solution under constant irradiance. Thus, the reaction will be first-order with respect to P. The \([\text{transient}]_{\text{tr}}\) can be calculated from the observed first-order rate constant, \(k_{\text{obs}}\) by:

\[
[\text{transient}]_{\text{tr}} = \frac{k_{\text{obs}}}{k_p} \tag{1.4}
\]

When possible, such rate expressions will be used to model that data generated from this research.

1.4 Rationale for Present Research

Although recent studies (Vaughn and Blough, 1998; Canonica et al., 2000; White, 2000; Sanvik et al., 2000; Algeria et al., 1999; Paciola et al., 19XX; Andrews et al., 2000) have concentrated on identifying and quantifying specific reactive transients generated from photochemistry of natural waters, little has been done by way of actually testing wetland waters in their ability to photochemically degrade NPS pollutants (Mabury et al. (2000) presented one of the few studies in this research area.) Instead,
most studies are content with performing "back-of-the-envelop" calculations (Brezonik and Fulkerson-Brekken, 1998) or applying environmental fate models (Arbrust, 2000) to estimate expected degradation rates. While such calculations are useful, they overlook the fact that for a given water, a change in even one parameter can vastly affect the photoreactivity toward contaminant degradation. In fact, little has been done in investigating how the spatial variability in composition in "flow-through" aquatic systems can affect such processes.

Thus, the current knowledge of photochemical processes occurring in wetlands lacks understanding in how natural water constituents can act synergistically and/or counter to one another to affect contaminant degradation. Probing wetlands for constituent-promoted reactions may provide information on how naturally occurring photosensitizers may be used to remediate NPS pollutants in these aquatic systems. By assessing the photochemical contribution to the degradation of select organic contaminants in various wetland waters, this research may provide additional information to describe how wetlands may act to enhance the quality of surface waters.

1.5 Research Goals

The major goal of my dissertation research is to ascertain the potential for NPS pollutants to be transformed by photochemical processes in wetland waters.

Specifically, the goals of this research include:
• characterizing the photochemical properties of NOM in various wetland surface waters. The primary means of accomplishing this goal was through the use of UV/VIS spectrophotometry in studying the spectral changes that occurred during irradiation of natural water samples and isolates and to assess how these properties correlated to contaminant degradation (Chapter 4).

• probing the ability of wetland water constituents to promote target agricultural NPS contaminant (carbaryl and alachlor) degradation. Through the use probes and alteration of reaction conditions, the identification of important reactive intermediates and their precursors were identified (Chapter 2 and 3).

• quantifying the dynamic contribution of these processes to the removal of non-point source pollutants from waters passing through a wetland. Both site-specific and temporal trends were identified and evaluated for the degradation of carbaryl in Old Woman Creek Water (Chapter 2).

The specific objectives of this research include:

• quantifying and qualifying the dissolved natural organic materials found in specific agricultural wetland sites (Old Woman Creek Estuarine Reserve; Fulton, Defiance, VanWert, and Champaign Counties (Ohio) Wetlands);

• elucidating and evaluating the role of direct and indirect photolyses in the degradation of some commonly used agrochemicals in polychromatic light representative of the solar spectrum. Carbaryl (Chapter 2) and alachlor (Chapter 3) were targeted for this study because of their ubiquitous use in Ohio agriculture;
• conducting photodegradation experiments in the presence of NOM isolated from wetland field sites (Old Woman Creek and Fulton County Wetland NOM);

• studying the role of several well characterized humic substances in the indirect photolysis of the target compounds. Experiments were performed with NOM isolates (Suwannee River Fulvic Acid and Lake Frxyell Fulvic Acid). These materials have been well characterized in the literature and therefore, serve as an excellent basis for comparison of the results presented here to other literature studies; and

• relating wetland NOM type (origin) to specific photochemical properties.

1.6 Anticipated Results and Benefits

This research will advance understanding of the photochemical processes that control the fate of pollutants in wetland surface waters. The research is expected to provide significant information regarding the participation of common wetland water constituents in the indirect photoreactions that affect the fate of chosen contaminants. Additionally, the results from this research will further elucidate the role of wetlands in providing a “buffer zone” to enhance the water quality of streams that enter receiving waters. Because of current interest in the restoration of wetlands, understanding
photochemical mechanisms that control the transformations of pollutants is critical to ascertaining a wetland's effectiveness as "photochemical reactor".

The results from this research could be used to update currently proposed models for the transformation of compounds in wetlands (Rodgers and Dunn, 1992; Burns, 1997). However, because these experiments are primarily performed in the lab, care must be used when applying measured rate constants to models used in the field. Numerous environmental factors such as turbidity, poor basin mixing, and vegetative cover can significantly affect transformation rates. These concerns are important and eventually need to be addressed but are beyond the scope of this research. The information generated from this research will provide an "upper-end" approximation of expected reaction rates in the field and may provide guidance in the design of wetland basins to be used for the remediation of contaminated waters collected from agricultural watersheds (i.e., for pilot-type studies).
A: natural water constituent capable of absorbing photons

\( r = k_A [A] \Phi_i \)

\( k_A \): specific light absorption rate constant

\( \Phi_i \) = primary quantum yield at wavelength j

\( X_i \): photogenerated reactive transient

P: solute (pollutant or transient probe)

\( k_{x,p} \) = rate constant for reaction of P with \( X_i \)

Figure 1.1 Direct and indirect photolytic processes occurring in natural waters (adapted from Hoigné, 1990).
CHAPTER 2

PHOTOCHEMICAL TRANSFORMATION OF CARBARYL PROMOTED BY NATURAL WATER CONSTITUENTS IN A WETLAND SURFACE WATER SAMPLED FROM AN AGRICULTURAL WATERSHED

2.1 Introduction

Non-point source pollution from surface runoff contaminated with agrochemicals threatens communities that rely on surface water for their drinking water supply and recreation. Four times more waters were reported to be polluted from agricultural chemical runoff than from municipal sources (U.S. EPA, 1992; Baker, 1993). For example, a long-term study that monitored agrochemical concentrations in seven Lake Erie tributaries in Ohio from 1983-1991 indicated that monthly average concentrations of atrazine and alachlor generally exceeded maximum contaminant levels (MCLs) for at least one month following herbicide application (Richards and Baker, 1993).

Wetlands may provide a means of managing water quality since water from diffuse surface sources may collect in wetland basins before final discharge to receiving waters. Several physical characteristics of wetlands suggest that they could be efficient photochemical reactors. Wetlands generally have large surface areas and shallow depths that would allow significant sunlight exposure and penetration throughout the water
column. Recent evidence suggests that photolysis is an important degradative pathway for many agrochemicals. Field studies conducted in streams and rivers located in Iowa have shown that an increase in the number of sunlight hours (from winter to summer) results in a significant increase in the overall transformation coefficient (by as much as a factor of four) for atrazine (Kolpin and Kalkhoff, 1993). The photolytic degradation of several pesticides (and daughter products) was significant in rice fields, and the effect was attributed to the concentration of contaminants in surface microlayers (Geyer et al., 1996) and photosensitized reactions (Mabury and Crosby, 1996).

Contaminants can be degraded by both direct and indirect photolysis (Kolpin and Kalkhoff, 1993; Simmons and Zepp, 1986; Hwang and Hodson, 1987; Woodburn et al, 1993; Blough and Zepp, 1995). Wetlands, in comparison to other water bodies, are rich in photosensitizers such as natural organic matter (NOM) and total nitrates for those systems located in agricultural watersheds both of which are capable of absorbing sunlight and catalyzing the transformation of organic compounds via indirect pathways (Blough and Zepp, 1995; Hoigné, 1990). NOM is comprised of labile decomposed organic matter and/or extracellular products as well as non-labile humic substances. Both pools of organic matter may contain a variety of chromophores (Valentine and Zepp, 1993) capable of acting as photosensitizers. Total nitrates (i.e., nitrate and nitrite) are another important class of photosensitizers in natural waters and are the dominant precursors in photoinduced production of the chemically reactive hydroxyl radical (HO\(^\cdot\)) (Haag and Hoigné, 1985; Mabury and Crosby, 1994; Torrents et al., 1997). While nitrate levels are typically low in many natural waters (< 10 \( \mu \)M), they are often elevated in
wetlands receiving agricultural runoff after precipitation events (Zepp and Hoigné, 1987). Thus, indirect photolysis may be an important degradative pathway in these wetlands for those contaminants that are incapable of absorbing solar radiation.

The focus of this research is to provide an understanding of the photochemical processes occurring in a wetland surface water and to evaluate the influence these processes have on the transformation of the pesticide carbaryl (1-naphthyl-N-methyl carbamate). This compound was chosen because it is a widely used phenyl N-methyl carbamate insecticide in Ohio and across the United States (USGS, 1993) which can undergo direct and indirect (through its reaction with HO*) photolysis (Mabury and Crosby, 1996; Zepp and Cline, 1977; Karinen et al., 1967; Samanidou et al., 1988; Armbrust and Crosby, 1991). Specific objectives of this research were to identify the photoreactive constituents (NOM and nitrates) in a freshwater wetland and to elucidate the role that these constituents play in the indirect photolysis of carbaryl.

2.2 Material and Methods

2.2.1 Chemicals and Reagents

All chemicals and reagents were purchased commercially and used without further purification. Purchases were as follows: Carbaryl from Chem Services (99%; West Chester, Pa), 1-Naphthol from Aldrich (99%; Milwaukee, WI), Chemical reagents
(potassium dihydrogen phosphate, potassium phosphate, sodium borate, trace metal grade sulfuric acid) and HPLC solvents of the highest purity from Fisher Scientific (Chicago, IL). Purified water was produced from a Milli-Q water system (Millipore Corp., Bedford, MA).

2.2.2 Collection and Characterization of Wetland Raw Water

The field site selected for sampling wetland surface water was Old Woman Creek Estuarine Reserve (OWC) which is a 30 hectare wetland located on the south shore of Lake Erie, 5 km east of Huron, OH (Figure 2.1). Approximately 69 km² of agricultural land drains into OWC's basin and subsequently, it receives a significant amount of suspended solids and pesticides (D. Baker, personal communication). Sampling sites were chosen at the inlet, interior (railroad), and outlet of the wetland. Sampling from the actual interior was prevented due to our deference to the preservation efforts protecting nesting habitats of bald eagles present at our sampling site. Samples were collected in June (which corresponded to the time of spring runoff: Kreiger, personal communication), August, and September of 1998. Raw water samples were collected in 4-L amber glass jugs, placed on ice, and transported to OSU. Samples were stored at 4°C until use.

Wetland water samples were filtered through a glass fiber filter (Gelman A/E) prior to analysis and use. Samples were analyzed for total organic carbon (TOC) using a Shimadzu TOC 5000 Analyzer. The light absorbing properties of the TOC were assessed by UV/VIS spectrophotometry (Varian Cary 1). Samples were scanned in a quartz
cuvette from 200 to 600 nm. The collected absorptivities were used to calculate attenuation coefficients and light screening factors appropriate for each natural water sample. Samples were analyzed for nitrate, nitrite, chloride, and sulfate via ion chromatography (IC) (Dionex DX-500 IC; Sunnyvale, CA). Twenty microliters of natural water sample were injected onto an IonPac AS-11 column (Dionex). A gradient method was used for ionic separation which entailed ramping the mobile phase (85:15(%v/v) H₂O :NaOH (0.021 M)) to 15:85 (%v/v), respectively, over a 20 minute period. The limit of detection for nitrate in the water samples was at 1.0 × 10⁻⁷ M.

2.2.3 Photolytic Reactions

Photochemical experiments were conducted using a merry-go-round reactor equipped with a xenon arc lamp (450-W) housed in a borosilicate immersion well (Ace Glass; Vineland, NJ) which screened out light with λ < 290 nm. Previous work has demonstrated that light emitted from xenon arc lamps closely approximates solar radiation (Yager and Yue, 1988; Leifer, 1988). In order to accommodate the xenon arc lamp, the merry-go-round reactor was modified according to our specifications. Cooling was achieved by circulating cold water through the immersion well and placing a fan above the lamp. The temperature of the reactor was 40°C during the course of these experiments. Light intensity was monitored with chemical actinometry (p-nitroanisole/pyridine system) (Dulin and Mill, 1982) and found to be 99.4% of summer sunlight (35°C) measured in Columbus, OH at a latitude of 40°N. During the course of
the experiments, the lamp intensity varied no more than 5%. Therefore, we assumed a constant light intensity was generated in our photoreactor during the course of the experiments and allowed us to compare observed rate coefficients directly without the incorporation of a correction term for variable light intensity.

Reaction mixtures were prepared according the following procedure. An aliquot of carbaryl stock solution (0.01 M in acetonitrile) was plated-out onto a graduated storage bottle. All traces of acetonitrile were evaporated under a gentle stream of argon since indirect photolytic processes can generate intermediates that may react with the acetonitrile (Canonica, personal communication). A pre-determined volume (for a desired concentration of approximately 5 μM carbaryl) of natural water sample or buffered MilliQ water (Millipore Corp., Bedford, MA) was added to the storage bottle and equilibrated for a few minutes. Studies showed that no longer than 5 minutes was necessary to completely re-dissolve the carbaryl plated on the walls of the bottle. The reaction solution was pipetted into pyrex culture tubes (13×100 mm) which were either placed in the photoreactor for irradiation (operated at 40° C) or in a temperature-controlled a water bath for the dark control (also at 40° C). Because of the high temperature, test tubes were completely filled as a precaution to avoid extra losses to the headspace due to Henry’s Law partitioning and solvent evaporation. In order to distinguish between direct and indirect photolytic mechanisms and a facile dark reaction, reactions were carried out at the pH of the natural water sample and in samples whose pH’s were adjusted to around 4.3. Test tubes were sacrificed periodically, and 20 μLs of
2 N HCl was added to each sample tube to reduce the pH to around 2.3, which completely quenched any dark reaction.

All samples from time courses were assayed by HPLC for the parent compound and the detectable derivative (1-naphthol). A direct aqueous injection (25 μL) from each vial was made into the HPLC and analytes were detected with a programmable fluorescence detector (Waters 470). The mobile phase for the analysis was 40% acetonitrile : 60% MilliQ water, and the flow rate was 1.0 mL/min. The program for the detector was: initial through 8.9 minutes, $\lambda_{\text{excitation}} = 282$ nm, $\lambda_{\text{emission}} = 330$ for carbaryl (RT = 3.4 minutes); 8.9 minutes through 11 minutes, $\lambda_{\text{excitation}} = 292$ nm, $\lambda_{\text{emission}} = 462$nm for 1-naphthol (RT = 4.5 minutes). Preliminary work in our lab has shown that this analytical approach is highly sensitive and provides linear detection over several decades of analyte concentration.

2.2.4 Fluorescence Lifetime Measurements

Fluorescence lifetime measurements were made by Xin Tan using Time-Correlated Single-Photon Counting (TCSPC) in the laboratory of Dr. Terry Gustafson, Department of Chemistry, OSU. The equipment used was previously described in detail (Danielson, 1995). The excitation wavelength used was estimated to be approximately 290 nm and emission was monitored at 334 nm for carbaryl and 467 nm for 1-naphthol. Data were analyzed by the iterative re-convolution of single exponential decay curve with the instrument’s response function. The response of the instrument was measured at full-
width half-maximum and was approximately 50 ps; thus, the instrument had the ability to resolve events above 10-20 ps (Xin Tan, personal communication).

Samples were prepared for TCSPC as follows. A volume of carbaryl stock solution (acetonitrile) was delivered to a four-sided quartz cuvette using a Chaney adapter in an amount necessary to obtain a concentration of carbaryl in the cuvette close to the expected aqueous solubility ($\sim 2.0 \times 10^{-4}$ M) when 3.8 mL buffer was added. A stream of argon was used to evaporate the acetonitrile prior to buffer addition. The buffer solution (sparged with argon for at least 30 minutes) was transferred to the quartz cuvette using a gas tight syringe under stream of argon. The final solution was further sparged with argon for one minute prior to analysis. Buffers were prepared from phosphate (5 mM), and pH adjustments were made with either 0.01 M HCl or 0.01 M NaOH. Since carbaryl is degrades to 1-naphthol through dark pathways, it is necessary to test for interference of the fluorescent signal from the presence of 1-naphthol. At 23°C (the ambient temperature of the lab where the experiments were performed), the second-order rate constant for transformation carbaryl by $\text{OH}^-$ to form 1-naphthol is 204 M$^{-1}$min$^{-1}$ (Aly and El-Dib, 1971); therefore, this reaction would produce a concentration of 1-naphthol of $9.58 \times 10^{-6}$ M in about 30 minutes. A $2.0 \times 10^{-5}$ M solution of 1-naphthol was used to test for interference (Data for the TCSPC is generally collected over 10 minutes, so this concentration includes a large safety factor). The lifetimes of carbaryl and 1-naphthol were tested at a low (4.33) and high (9.04) pH.
2.2.5 Data Analysis

Kinetic data from photolytic timecourses were analyzed using *Scientist for Windows* v. 2.01 (MicroMath Scientific Software, Salt Lake City, UT). Rate expressions describing the observed kinetics were solved numerically using the EPISODE package, and observed rate constants for carbaryl degradation were determined from least squares fit (Powell algorithm) of the observed kinetic data to the pseudo-first order kinetic model. I did not consider it necessary to correct for carbaryl binding to dissolved organic matter since carbaryl has a relatively high solubility (0.05 g/L @ 20°C), and calculations based on the published organic carbon partitioning coefficient (205-457 L/kg; Mackay *et al.*, 1992) showed that no more than 0.7% of the carbaryl present in the solutions would be associated with the organic matter present in the OWC water.

2.3 Results and Discussion

2.3.1 Natural Water Characteristics

Several water quality parameters (*e.g.*, pH, TOC (a measure of the NOM content), nitrate, alkalinity) were measured for the OWC samples (Table 2.1). The UV/VIS absorption spectrum for each OWC sample was also recorded (Appendix A, Figures A.1-10). The spectra of the June samples were dominated by the presence of nitrate (see insert in Figure A.1) as expected based upon the measured concentrations of nitrate in
these samples (Table 2.1). For the August and September samples, spectra more characteristic for NOM present in natural water samples were obtained.

Normalized (to the total amount of carbon present) molar absorptivities ($\varepsilon$) at $\lambda=280$ nm may indicate the amount of aromatic carbon present in natural water samples (Gauthier et al., 1987; Traina, 1990; Chin et al., 1994). The low molar absorptivities (corrected for nitrate absorbance at $\lambda = 280$ nm) observed for OWC water suggests that this material contains few aromatic moieties (Figure 2.2A; Table 2.1). As a comparison, International Humic Substance Society (IHSS) fulvic acids isolated from “blackwater” swamps possessing high aromaticity (e.g., Suwannee River) have extinction coefficients at $\lambda = 280$ nm that are at least 2x's greater than those measured here (Chin et al., 1994). Moreover, even though the amount of NOM varies during the summer season, at all sites between June and September, $\varepsilon$ remains approximately the same (except for the major spike occurring at the end of June) (Figure 2.2A). Thus, the input of new organic matter over time appears to be similar in aromaticity. The normalized absorptivity, however, does decrease slightly for both sample sets from the inlet (railroad) to the outlet and suggests that the aromatic character of the organic matter changes as water passes through the wetland (Figure 2.2A). The railroad site has similar absorptivity to the inlet, not wholly unexpected because of the proximity of the two sites (Figure 2.1). This phenomenon may be caused by the selective removal of aromatic moieties to mineral oxides in the water column followed by subsequent sedimentation (Chin et al., 1998).
Moreover, decreases observed in the OWC organic matter absorptivity may also be caused by photobleaching as the water passes through the wetland. Such an interpretation would be supported by recent literature, which reports the selective photolability of phenolic functional groups (lignin-derived) in soil NOM dissolved into water (Schmitt-Kopplin et al., 1998). I expect that much of the aromatic functional-group input to the wetland surface water results from runoff carrying leached soil NOM and from decaying leaf litter of water lilies which are prolific in the wetland from July to August. It is not known what the relative contributions of each source are. However, the correspondence of the ε<sub>280</sub> spike (Figure 2.2A) to spikes in nitrate (Figure 2.2B) and total iron (Figure 2.2C) measured in the inlet water of wetland suggest that soil NOM contributes a significant portion.

Simple mixing may also account for the changes in the molar absorptivity. Runoff entering an aquatic system that is characterized by a high microbial or algal productivity will produce an organic matter of a different functionality ratio (aromatic: aliphatic) than terrestrial (mostly lignin derived) organic material (McKnight and Aiken, 1998). The observation an overlap in ε<sub>280</sub> between all sampling sites during certain times of the summer season indicated that mixing can be an important process in governing ε<sub>280</sub>. Overall, the values presented here agree with NOM molar absorptivities measured from rivers where the NOM is derived from both autochthonous and allochthonous sources.

Previous results indicated that direct photolysis of carbaryl between λ = 290-370 nm may be a very efficient process (Armbrust and Crosby, 1991). Since the objective in
this study was to identify the wetland water constituents participating in indirect photolytic processes, I chose to study photolysis at two pH's. First, I wanted to observe the reactivity of the water samples at the natural pH of this wetland surface water. Second, I reduced the pH of the water samples (to a pH of 4.3) in order to minimize the kinetic interference from the base-catalyzed dark pathway. At the naturally occurring pH of the OWC samples (around 8; Table 1), the dark reaction was significant enough to hinder my ability to ascribe the reactivity to photolytic pathways. In observing the reactivity at these two pH's, I found that pH became a very important factor in determining the kinetics and mechanism through which this compound can be transformed in natural waters. Moreover, my findings also have some important implications regarding the photodegradation of other phenyl-N-methyl carbamates in natural or NOM fortified waters reported in the literature (Bachman and Patterson, 1999) and justifies the re-interpretation of the published results.

2.3.1.1 Light Screening Factors

Since the UV-VIS spectra were recorded for each water sample, it was possible to calculate the light screening factor as a function that varies with wavelength (Table 2.1). A light screening factor \( S_\lambda \) can be used to correct for the inhibition that light attenuation by natural waters has on the direct photolysis rate of a contaminant \( C \) at a particular wavelength (Leifer, 1988). Application of \( S_\lambda \) to rate constants measured in distilled water can yield upper-limit estimates of expected direct photolysis rates in the natural waters.
under identical irradiation conditions. The light screening factor at a specific wavelength \( \lambda \), \( S_\lambda \), can be calculated from the equation

\[
S_\lambda = \frac{1 - 10^{-\alpha_\lambda l}}{2.303 \alpha_\lambda l}
\]

where \( l \) is the pathlength of the test tubes used for the experiments (1.12 cm; Zepp et al., 1978; Leifer, 1988) and \( \alpha_\lambda \) is the light attenuation coefficient for natural water constituents (the measured absorbance for a given wavelength when the cuvette pathlength is 1 cm). This equation is valid only in systems where the attenuation due to the natural water constituents is much greater than the attenuation of the contaminant \( (\varepsilon (M^{-1}cm^{-1}) \times [C] (M)) \) of interest. Since the xenon lamp (polychromatic light source) was used to irradiate the natural water samples, an overall screening factor, \( S_{\Sigma} \), for all the wavelengths that could be absorbed by carbaryl (290-370 nm) was calculated. First, the \( S_\lambda \) for the natural water samples at each wavelength present in the solar spectrum (\( \lambda = 290-700 \) nm) was determined from the measured absorbance. A value of 1.0 for \( S_\lambda \) indicates complete light transmission through the sample. The resulting values were plotted versus wavelength (Figure 2.3). A 4\(^{th}\) order polynomial was fit (Least squares, Microsoft Excel) to the plots yielding an equation that adequately \((R^2=0.99)\) described the screening factor as a function of the wavelength in this range. This was done for each natural water sample in which an experiment was run \((i.e., \text{pH}=4 \text{ and pH}=8 \text{ samples})\). These equations were then integrated and evaluated from \( \lambda = 290-370 \) nm to yield the area under the curve, which represents the light available to carbaryl for direct photolysis after attenuation from the...
natural water constituents. The areas were then normalized to the area expected if no screening was occurring (i.e., constant $S_x=1.0$) to yield the overall screening factor ($S_{\Sigma}$).

For the water samples, $S_{\Sigma}$'s ranged from roughly 0.84-0.98 depending on the water sample (Table 2.1; Figure 2.3) and suggest that light attenuation by natural water constituents could compete for up to 19% of the photons impinging the samples in the laboratory experiments. In contrast, if I consider the attenuation of carbaryl (at 8 $\mu$M) in the region where it absorbs light significantly (i.e., 290-370 nm), the calculated screening factor (approximately 0.997) indicates that carbaryl would compete for less than 1% of the photons impinging on the sample.

2.3.2 Reaction Kinetics

The values obtained from the screening factor calculations also indicate that both the direct and indirect processes and hence, kinetics, would not be photon-limited. Thus, if both processes occur significantly, these processes will conform to pseudo-first order kinetic models (Liefer, 1988). In systems where photons are not limited, the direct photolysis rate for a dilute solution of contaminant (i.e., $C \ll \alpha$), $C$, is expressed as:

$$\frac{dC}{dt} = -\phi_{dp} I_0 \left( \frac{A}{V} \right) F_s F_e$$ (Zepp and Cline, 1977; Zepp, 1978)

where the rate of transformation of contaminant, $C$, is directly proportional to the initial light intensity ($I_0$) multiplied by the fraction of light absorbed by the system $F_s$ (where $F_s=1-10^{(\alpha \lambda + \alpha L \lambda)}$ and $l$ is the reaction cell pathlength), the fraction of light absorbed by the
compound of interest \( F_c \) (where \( F_c = \frac{eC}{(\alpha + \varepsilon)C} \)), the cell geometry (Area:Volume ratio), and the quantum yield for the direct photolysis transformation reaction \( \Phi_{dp} \) of \( C \).

According to the above equation, the direct photolysis rates are predicted to vary significantly from one sample to the next in proportion to the attenuation of light by the natural water constituents in the system when \( \alpha > 0.02 \). The effect of constituent light screening is to remove photons out of the system thereby decreasing the light intensity available for direct photolysis. Only in the case where the attenuation coefficient of the natural water constituents, \( \alpha \), is less than 0.02 will the specific rate of light absorption by \( C \) be constant and independent of \( \alpha \) (see discussion in text of Zepp and Cline, 1977). Likewise, the rate for contaminant degradation due to indirect photolysis can also be quantified according to a pseudo first-order model in that under constant irradiation, a stationary state of reactive intermediates will be established.

These terms from the direct and indirect photolysis and any significant dark reaction may be collected into an overall rate expression for the degradation of the pollutant of interest. Thus, the contribution of any known environmental process to the observed first-order rate coefficient for carbaryl’s disappearance \( (k_{\text{obs}}) \) may be quantified by comparing the relevant first order or pseudo-first order rate constants for the process in question \( (k_i) \) to the sum of the relevant rate constants \( (\Sigma k_j) \):

\[
k_{\text{obs}} = \Sigma k_j = k_{OH^+} + k_{\text{direct}} + \Sigma k_{\text{transient}}
\]

\[ (2.1) \]
where \( k_{OH^-} \) is the second-order rate constant for the base-promoted elimination reaction, \( k_{direct} \) corresponds to the relevant rate coefficient for the direct photolysis, and \( \Sigma k_i \) are the second-order rate constants for any reactive transient species \( i \) that results in the indirect photolysis of carbaryl. The literature has shown that the true hydrolysis of carbaryl by \( H_2O \) is insignificant; likewise, at the pH of the natural waters, an acid catalyzed pathway is negligible (Aly and El-Dib, 1971a,b; Wolfe et al., 1978).

The results from the time courses run in these experiments were treated according to pseudo-first-order kinetics, and the models fit reasonably well having an \( R^2 > 0.99 \) for all reactions (e.g., Figures A.11-31 in Appendix A). The dark reaction for carbaryl in the natural waters with the unadjusted pH was shown to be quite significant when compared with the reaction in the light (Figure 2.4; Table 2.2). In contrast, the dark reaction for carbaryl in the pH-adjusted samples was insignificant compared with the light reaction and the reaction carried out in the dark at the higher pH (Figure 2.5; Table 2.2). This result is not unexpected since carbaryl is known to undergo a significant base-catalyzed elimination reaction at pH's greater than 7 (Aly and El-Dib, 1971a,b; Wolfe et al., 1978).

According to the analysis of the data, the contribution from the elimination pathway was large in the unaltered samples and, in fact, accounted for the largest percentage (ranging from 46-73%) of the overall reaction in the presence of light (Table 2.2). The light induced degradation of carbaryl, however, in the higher pH samples was not insignificant. In fact, light was found to promote the transformation by 1.5 to 2.2 \( \times \)'s for the natural water samples (Table 2.2). Thus, the presence of light did enhance carbaryl's degradation. The only daughter product observed and quantified under our
analytical conditions was 1-naphthol (Figure 2.6). In the dark reactions, 1-naphthol accumulated in the reaction solution resulting in good mass balances (Figure 2.6; Table 2.2). Conversely, in the photoexperiments, 1-naphthol behaved as a photoreactive intermediate and never accumulated to levels observed in the dark, and mass conservation based on this derivative alone was never achieved (Figure 2.6; Table 2.2).

In the pH adjusted natural water sample, the reaction in the light accounted from 87 to 98% of the overall reaction (Figure 2.7; Table 2.2). The daughter product, 1-naphthol was not detected under our analytical conditions; hence resulting mass balances were poor. The dark reaction was relatively insignificant at the lower pH experiments and accounted for as little as 1 to at the most 13% of the overall reaction. Thus, these two independent results provide strong evidence that dark pathways for carbaryl transformation were insignificant at this pH.

In summary, from 32-98% of the overall degradation reaction observed in both unaltered and pH adjusted natural water samples could be attributed to light induced pathways (direct and indirect). In addition, regardless of the pH, the light promoted degradation of carbaryl occurs at a similar magnitude (Figure 2.8). This result indicates that light is an extremely important factor in the degradation of carbaryl, and, suggests that it will play an important role in governing the fate of carbaryl in the environment. What remains is to identify and delineate which photochemical processes are primarily responsible for the transformation of carbaryl in the light.
2.3.3 Direct Photolysis

The "hydrolysis" of carbaryl in the dark has been well studied and occurs according to a base-catalyzed elimination reaction. (Aly and El-Dib, 1971b; Wauchope and Haque, 1973) (Figure 2.9).

Direct photolysis of carbaryl at pH > 7.0 has not been well-studied, even though several studies suggest a pH promoted pathway (Aly and El-Dib, 1971b; Wauchope and Haque, 1973; Pramauro et al. (1998)). The definitive evidence supporting this suggestion has not yet been provided. In fact, based upon the literature, a strong case could be made for assuming that carbaryl's direct photolysis is not pH dependent. Wolfe et al. (1978) found that the quantum yield for direct photolysis was independent of pH at pH's <7.0. Other researchers have reported a directly proportional pH dependency of carbaryl photolysis (Aly, O.M. and M.A. El-Dib, 1971b; Pramauro et al., 1997) but failed to correct their data for the pH dependent dark reaction (i.e., base-catalyzed elimination reaction). For example, Pramauro et al. (1997) present data (Figure 2 of that paper) that show a pH dependency on the extent of the direct photolysis of carbaryl. They mention in the text that dark controls did not show an appreciable degradation at the tested pH's (though it is not specified in the paper how the dark reaction controls were performed). If one calculates a dark reaction rate coefficient for their experimental conditions (55° C during Xenon lamp operation) from an Arrhenius plot of previously reported base-catalyzed elimination constants (Wauchope and Haque, 1973; Wolfe et al., 1978), a large
portion of the observed degradation of carbaryl can be accounted by the dark reaction at this pH and temperature (i.e., at pH = 9.0, \( t_{1/2} \), calculated = 15 minutes).

Furthermore, Pramauro et al. (1997) present some UV/VIS absorption spectral data (inset, Figure 2 of that paper) showing a supposed bathochromic shift of carbaryl's absorption from \( \lambda = 290 \) to 330 nm when the solution pH was varied from a pH =3 to 9. They attribute the observed pH dependency of the direct photolysis to the change observed in the absorption spectra. They argue that the change in the UV/VIS absorption spectra results in a promotion of direct photolysis due to the more energetically accessible (because of the shift to lower energy) excited states. No details, however, were divulged as to how these UV/VIS measurements were made.

I repeated the UV/VIS measurement of the absorbance spectra of carbaryl in the pH range of 6-9 using an experimental procedure designed to minimize the time between sample mixing and analysis (Figure 2.10). In my procedure, 3.4 mL of buffer solutions (varying in pH from 6-9) were added to quartz cuvettes (pathlength = 1 cm). This pH range was chosen because it is where the direct photolysis was most sensitive to changes in pH and thus, where most changes should occur in the absorbance spectrum if it is pH dependent. A spike of 150 \( \mu \)L of carbaryl in acetonitrile was added to the sample in the cuvette. The cuvette was capped, and inverted 4 times to promote mixing and the UV/VIS absorption spectrum was taken immediately (within 30 seconds of mixing). Using scan rates of 200 nm/min (~ 1.0 minute per scan), the entire process was completed within 1.75 minutes from the time of mixing. These considerations are important because at the higher pH buffers, the base-catalyzed elimination reaction can be quite significant.
For example, at a pH of 9, I detected the growth of the daughter product, 1-naphthol, spectrophotometrically within 30 minutes of mixing (Figure 2.11). Appropriate controls were performed: a UV/VIS scan of acetonitrile confirmed that there would be no interference in the wavelength regions scanned, i.e., 250-450 nm. Also, all buffers were tested prior to carbaryl spiking to ensure that differences between reference and sample cells were minimal (i.e., that the reference cell was adequately compensating for the buffer and that the cells had not been contaminated between samples). Contrary to Pramauro et al. (1997), the results showed that there was no significant difference in the UV/VIS absorption spectra in these pH ranges (Figure 2.10). As a result, I believe what these authors observed an experimental artifact caused by allowing their solutions to sit too long before measuring the UV/VIS. The base-catalyzed elimination reaction is quite efficient at this pH and our results from this experiment showed that within 30 minutes a significant amount of 1-naphthol accumulated in solution and interfered with the UV/VIS absorption spectrum (Figure 2.11). After 2.5 hours, the spectrum of the pH=9 carbaryl solution, now composed of 26% 1-naphthol, provides an almost identical match to the spectrum reported in Figure 2 of Pramauro et al. (1997). These results suggest that these authors measured the absorbance of a solution composed of 1-naphthol and carbaryl and that there was no basis for their assertion that differences in the UV-VIS absorption spectra were responsible for the enhanced photoreactivity at the higher pH.

Therefore, based on the literature at this time, there is no substantial evidence to support that there is a pH dependency of the direct photolysis of carbaryl at environmentally relevant wavelengths, and so, it is necessary to definitively determine
whether or not this phenomenon was occurring. Since carbamate pesticides are widely used pesticides, and the pH varies tremendously between natural waters, a pH dependent photolytic mechanism could have tremendous implications regarding the fate of N-methylcarbamate pesticides in natural waters, especially for those waters that are highly alkaline.

2.3.3.1 Effect of pH on the Direct Photolysis

In order to investigate a pH-dependent photodegradation of carbaryl, carbaryl was irradiated at several pH's ranging from 6-8.5 with $\lambda=365$nm light (200-W Mercury Arc Lamp fitted with filters to screen out other wavelengths). Rate coefficients and quantum yields measured were found to correlate positively to the pH (Figures 2.12, 2.13). The extensive difference measured for carbaryl's direct photolysis rate coefficients (at least an order of magnitude) between a pH of 4.3 and 8 in the solar simulator (Table 2.2) suggests a variable impact of direct photolysis on the degradation of this compound in natural waters. While this dependency will not be significant at lower pHs (see inset Figure 2.13) in agreement with the observations of Wolfe et al. (1978), it may have a significant effect in enhancing carbaryl's direct photodegradation rate in more alkaline natural waters such as OWC.

The principal dark reaction product, 1-naphthol, can be a potential photosensitizer, and it's role in promoting the observed pH dependence on the direct photolysis pathway for carbaryl must be ruled out. Photochemical reactivity of 1-naphthol could influence
the fate of carbaryl through a number of mechanisms. First, as this daughter product accumulates, it may compete with carbaryl or other photoreactive water constituents for photons, thereby inhibiting carbaryl degradation. Conversely, evidence in the literature shows that 1-naphthol may act as a photosensitizer which could enhance carbaryl degradation. Control experiments were performed to test the effect of 1-naphthol on the degradation of carbaryl. In phosphate buffered solutions (pH=8.5), 1-naphthol was added at various molar ratios to a solution of carbaryl (5 μM) (Figure 2.14). There was no statistical difference between the rate coefficients measured for various mole ratios of 1-naphthol: carbaryl compared to the reaction without added 1-naphthol. Thus, 1-naphthol is not photosensitizing the degradation of carbaryl; therefore, the principal pH-dependent direct photolytic pathway is due to some other mechanism.

Considering these results along with the UV/VIS data and observations of the pH-dependent reaction suggest that an alternate direct photochemical mechanism is occurring in addition to the currently accepted direct photolytic cleavage mechanism which is reported in the literature for other N-methyl carbamates (Bachman and Patterson, 1999). The little difference observed in the UV/VIS absorption spectra for carbaryl at different pHs (Figure 2.10) suggested that a photochemically promoted second-order reaction could be the mechanism responsible for an observed pH dependency. Perhaps the difference in the direct photolysis mechanism is due to the fact that the homolytic cleavage mechanism was proposed for solutions of N-methyl carbamates that were irradiated with light of $\lambda = 254$ nm. This higher energy radiation may produce an electronic transition that is unrealistic for natural water systems where sunlight is of lower
energy (λ > 290 nm). The photochemistry in my systems will most likely be driven by lower energy transitions, such as a n-π*, which can occur for many molecules at wavelengths present in sunlight. Carbaryl has a maximum absorbance at 270 nm with a shoulder at 290 nm that tails off past 300 nm and includes two smaller shoulders at 310 and 315 nm (Figure 2.10). Thus, I would expect that a n-π* transition would be accessible to carbaryl in sunlight. The type of the transition occurring for carbaryl at relevant wavelengths (i.e., in the solar spectrum) can be assessed from published UV/VIS and fluorescence data (Table 2.3). For the peak at λ = 280 nm, a hypsochromic shift occurs as the solvent polarity is increased. This is indicative of a molecule having less of a dipole in its excited state than its ground state. A n-π* transition for carbonyl compounds would be consistent with this data; however, a π-π* transition cannot be completely ruled out since the absorption spectra were measured for solvents with a limited range of polarity (Table 2.3) and the presence of the aromatic group (naphthyl) may cause a red-shift in the absorption band of the π-π* which could make the transition accessible in solar wavelength region.

A few potential pathways exist for the reaction of carbaryl in the photoexcited state to undergo a base-promoted degradation. First, the pKa of the nitrogen could change significantly as a result of an excitation-induced polarization of a molecule. A π-π* transition occurring on the carbonyl could result in an excited state having an increased dipole compared to that of the ground state while an n-π* transition would cause an excited state with less of a dipole than in the ground state (Reichardt, 1979). A
change in the partial charge of the lower energy \( \pi \) orbital could significantly affect the pKa of the neighboring nitrogen. Conversely, a n-\( \pi^* \) transition of the non-bonding electrons on the nitrogen would render a more positively charged nitrogen center which could increase the acidity of the nitrogen. In general, phenols, amines, and protonated amines become more acidic while ketones, esters, carboxylic acids, amides, and azo groups become more basic in the excited state (Fleming, 1986). If the nitrogen in the carbamate became more acidic from excitation, then a rapid promotion of the base-catalyzed ground-state pathway would occur in the excited state. An increased dipole from a \( \pi-\pi^* \) would also intensify the partial positive charge on the carbon rendering it a stronger electrophile and more susceptible to nucleophilic attack. Either way, a base-promoted pathway must result from a bimolecular process. If the bimolecular process involves carbaryl in an excited state, then the reaction should dynamically quench fluorescence or phosphorescence and the observed lifetime of the excited state should decrease. Thus, by running fluorescence lifetime measurements on carbaryl in the aqueous solutions, a decrease in the measured lifetime (30 ns in aqueous solution; Wenska, 1997) should be observed if bimolecular quenching occurs in the singlet state. Lack of changes in carbaryl fluorescence lifetimes suggest either a bimolecular process in the excited triplet state, or by some other pathway.

Fluorescence lifetime data was collected on several samples (Table 2.4). Neither carbaryl nor 1-naphthol showed any pH dependency in the measured lifetimes (Figure 2.15, 2.16; Table 2.4). Controls showed that no interference would occur from the
presence of l-naphthol or the phosphate buffer on the lifetime of the carbaryl. From these experiments it could be concluded that the singlet state is not participating in a bimolecular reaction.

While the fluorescent lifetime data provides a picture of singlet reactivity in this system, it does not provide any information regarding triplet reactivity. Dissolved oxygen significantly quenches triplet states; therefore, reducing the amount of oxygen in solution through argon sparging should noticeably enhance the reaction if carbaryl is reacting from the triplet state. In order to evaluate the participation of the triplet state, a reaction was performed at high pH in air-saturated (pH 7.99) and argon-sparged solutions (pH 8.05) and compared (Figure 2.17). No significant difference was observed from what was predicted to occur at the measured pHs for all the samples (see section 2.3.1.5 for method of prediction). Therefore, it can be concluded that carbaryl is not reacting from the triplet state.

It is possible that the base-promoted reaction results from a facile proton transfer to the solvent occurring in the excited state. Proton transfers from excited states often occur on a timescale much faster (in the picosecond region) than that of relaxation of an excited state (Solntsev et al., 1999; Fleming, 1986; Zewail et al. 1996). Therefore, the lifetime of the excited state would not be affected by such a process. If such a process were occurring, then the molecular geometry would be different in the excited state from the ground state. Correspondingly, the emission spectrum will not mirror the excitation spectrum and a larger Stokes shift will occur for the compound. Both phenomena occur in the fluorescence spectra of carbaryl (Addison et al., 1977; Files and Winefordner, 1987).
Finally, the reaction could be promoted by a base outside of any excited state process. If there is a reversible reaction that occurs as an elementary step in the overall reaction that is dependent on [OH⁻], then presence of the base could shift the equilibrium toward products. For example, the hydrolysis of an isocyanate is catalyzed by bases (March, 1985).

2.3.3.2 Calibration of Photoreactor for Predicting Direct Photolysis Rates

Since the assumption cannot be made that the pH does not affect the direct photolytic pathway, we developed an empirical method for predicting what the direct photolysis of carbaryl should be in our xenon lamp system. The photodegradation reaction of carbaryl was measured at several pH's in buffered (phosphate and borate) MilliQ water. The k_corrected (hr⁻¹) vs. pH was plotted, and the resulting linear correlation was used to calibrate the expected pseudo-first order direct photolysis rate coefficient for a given pH in our xenon lamp photoreactor (i.e., k_dp (hr⁻¹) = 2.2 × 10³ × [OH⁻] + 1.4×10⁻³; n=4; R² = 0.993). Thus, for MilliQ water having a pH of 8.0, an expected direct photolysis rate coefficient would be 2.4×10⁻³ hr⁻¹. The light screening factor can then be applied to the predicted direct photolysis rate coefficients to yield a predicted direct photolysis rate for each natural water sample. These are listed in Table 2.2. By doing this, then, we can predict the quantity of carbaryl that can be transformed in the natural water due only to direct photolytic processes in the absence of other quenchers besides...
those that compete with carbaryl for photons. In this way, we have provided an upper-limit estimate of the direct photolysis rate coefficient.

2.3.4 Indirect Photolysis

Subtraction of $k_{\text{dark}}$ and $k_{\text{direct}}$ from $k_{\text{obs}}$ yields a pseudo-first order rate constant that is representative of the indirect photolytic processes (assuming that any other photo-promoted reaction is due to indirect photolysis mechanisms). The various contributions from direct and indirect photolysis to carbaryl’s enhanced photodegradation at the pH’s of concern can then be quantified (Figures 2.18, 2.19). The indirect photolytic processes may account from as little as 0% up to 97% the overall reaction in light depending on the pH. Likewise, depending on the pH, the direct photolysis accounts for as little as 3% to as much as 100% of the degradation enhancement observed in the light. These calculations demonstrate that indirect photolytic processes are primarily responsible for the observed photoenhancement in the pH 4 samples. At the higher pH samples, nearly all reactivity can be accounted for through direct processes. These results are significant for the following reasons: (1) there is a switch in the primary mechanism controlling carbaryl’s photolytic fate from a pH at 8 to pH at 4 from direct to indirect processes and (2) regardless of the mechanism, the photoenhancement occurs at approximately the same magnitude. While at the higher pH, the dark reaction is still the predominant mechanism controlling the degradation of carbaryl; at a lower pH, the indirect photolysis reactions become very important in influencing carbaryl’s fate in this wetland water.
In some of the waters at pH 8, the sum of the $k_{dark}$ and $k_{direct}$ exceed $k_{obs}$ (see negative values of indirect photolysis contribution in Figure 2.18). As I have pointed out previously, the application of screening factors to the direct photolysis rate coefficients in MilliQ water samples provides an upper-limit estimates of rates. Any other process occurring in the natural water not accounted for by application of the screening factor can compete with the direct mechanism thereby decreasing $k_{obs}$ and would explain the overestimation of $k_{obs}$. For example, I suspect that other constituents present in the water column may act to quench the chemical reaction of carbaryl excited states through unproductive photochemical processes (i.e., collisional deactivation). Since the direct photolysis pathway at pH=4 has effectively been “shut-down”, the effect of collisional deactivation does not apply to this system. In addition, the error associated with the experiments may also inhibit our ability to achieve equalities in these data manipulations.

An important lesson to be learned from my observation of the direct photolysis of carbaryl is that screening factors must be used with caution. Simply applying a screening factor to the rate coefficient determined from a control experiment in MilliQ water may not adequately predict direct photolysis rates, especially when control experiments are performed at a pH significantly different from that of the natural water of interest. For carbaryl, the predicted direct photolysis rate coefficient $k_{dp}$ becomes sensitive to changes in the pH at about pH=7, the region in which the pH for many natural waters falls (Figure 2.13). Thus, predicting the direct photolysis of compounds that behave similar to carbaryl, i.e., other carbamates, in natural waters is difficult without a priori knowledge of a direct photolytic mechanism. This finding may have important implications for the degradation
of other photochemically active N-methyl carbamates in natural systems. In addition, the role that the natural water constituents have in affecting the direct as well as indirect mechanisms must be considered and addressed.

Some important trends can be observed in the pH adjusted samples. First, the maximum photodegradation due to indirect processes occurs in the Inlet (6-29-98) water, the sample with the highest amount of nitrate (Table 2.1). Similarly, carbaryl transformation is less in the Railroad (6-29-98) and Outlet (6-29-98) samples in a trend that corresponds to the amount of nitrate present in the samples. The other samples, from August and September, show similar magnitudes of photopromotion even though they have at least an order of magnitude less nitrate present than the June samples. The Outlet (9-8-98) sample showed the least photopromotion and contained the least amount of nitrate and TOC (mg-C/L) (Table 2.1).

The possible reasons for the large range of reactivity in the pH-altered samples should be interpreted within the context of the water samples. Analysis of the surface water revealed two classes of constituents that may act as photosensitizers: total nitrates (i.e., the sum of nitrate and nitrite) and natural organic matter (NOM). Multiple regression of the pH=4 data indicated a significant relationship existed between $k_{\text{obs}}$, TOC, and nitrate level ($k_{\text{obs}}$ (min$^{-1}$) = 1.67 [NO$_3^-$] + 1.27×[TOC M-C/L] + 1.95×10$^{-4}$; $n$ =12; $R^2=0.97$) (Figure 2.20). While this relationship provides no information regarding the mechanisms for the indirect photolysis, it does show that the rate of reaction of carbaryl is positively correlated to the levels of nitrate and NOM present in the natural
water samples and may represent at least two photoinduced processes by which carbaryl is degraded.

2.3.4.1 **Total Nitrates**

A correlation between nitrate level and the normalized (to the amount of organic carbon) reaction rate coefficient (corrected for the dark reaction) was observed for the pH=4 samples only (Figure 2.21). The normalization of $k_{\text{corrected}}$ was performed to correct for the variation in $k_{\text{obs}}$ that would be due the scavenging and promotion effect of the NOM. The samples that showed the most significant light enhancement contained the highest levels of nitrate. The influence of nitrate had both a spatial and temporal variability on the rate coefficient (Figure 2.22). The observed pseudo-first order rate constant corrected for the dark reaction, $k_{\text{corrected}}$, decreased as nitrate level decreased through the wetland in the June samples (Inlet to Outlet) (Figure 2.22). In the August and September samples, occurring at a time when nitrate levels were significantly lower, and there was a corresponding decrease in the indirect photolysis of carbaryl.

Nitrate is capable of producing hydroxyl radicals (HO•) with quantum yields ranging from $9.0-17 \times 10^{-1}$ when irradiated at wavelengths between 290 and 330 nm (Zepp *et al.*, 1987; Mabury and Crosby, 1994; Fischer and Warneck, 1996; Jankowski *et al.*, 1999). Nitrite, a photolysis product of nitrate, can also produce HO• at quantum yields ranging from 0.015 to 0.08 between 298 and 390 nm, respectively (Zafiriou, O. C. *et al.*, 1987; Kieber and Jankowski, 1999; Mabury and Crosby, 1994; Fischer and Warneck, 1996).
1996; Arakaki et al., 1999). Under constant irradiation, the HO\textsuperscript{•} generated can react with other water constituents which results in a low, steady-state concentration of this reactive species. Carbonate species (HCO\textsubscript{3} and CO\textsubscript{3}\textsuperscript{2–}) and NOM are important scavengers of HO\textsuperscript{•} in natural waters (Larson and Zepp, 1988; Schwarzenbach et al., 1993; Bresonik and Fulkerson-Brekken, 1998; Lindsey and Tarr, 2000) and thus, will reduce the steady-state concentration of HO\textsuperscript{•} available for pollutant transformation. In wetlands that receive agricultural runoff, the nitrates may be sufficiently high enough to influence contaminant photolysis. Nitrates monitored in OWC from 1988-1990 ranged from 0.032-2.0 mM (Krieger, personal communication) and correspond well to this study (Table 2.1). In considering just the concentrations of nitrate measured in this study (1.3 \times 10^{-5}-1.01 \times 10^{-3} M), the production (noonday sunlight at 40° N latitude) of steady-state concentrations of HO\textsuperscript{•} in the OWC water in the presence of scavengers such as NOM and carbonate is predicted to be relatively high (~10^{-15}-10^{-17} M) (Eq. 13-62 from Schwarzenbach et al., 1993) when compared with that measured in other water bodies (~10^{-18}-10^{-16} M) (16). A value of 1.4 \times 10^{4} L/mg-C/sec was used for the rate coefficient for scavenging by NOM (Brezonik and Fulkerson-Brekken, 1998) was chosen because of similarity between the water in which this rate coefficient was measured and the OWC water, i.e., a highly productive, alkaline system.

One of the goals of this research was to understand the influence of scavengers in reducing the efficiency of the nitrate/nitrite promoted reactions in the OWC water. In order to accomplish this task, the photolysis of carbaryl was conducted at a wavelength (\lambda...
where the extinction coefficient and subsequent direct photolysis of carbaryl would be minimized and where attenuation of the natural water constituents (NOM) would also be minimized. While this wavelength is not considered an optimal choice for the indirect photolysis of carbaryl by total nitrate, nitrate and nitrite photolysis has been observed to occur at this wavelength (Jankowski and Keiber, 1999; White and Chin, unpublished data). I planned for these experimental conditions to favor nitrate/nitrite promoted indirect photolytic pathways over an NOM promoted process.

The light screening factor, $S_\lambda$ (corrected for the nitrates absorbance) was used to correct for the effect of light attenuation by other (than nitrate) natural water constituents on the photolysis rate at this wavelength ($\lambda=365$ nm). For the OWC water samples used in this set of experiments (June and August 1996), nitrate-corrected $S_\lambda$ ranged from 0.94-0.97 which suggests that light attenuation by natural water constituents would compete for only 3-7% of the photons impinging the samples in the laboratory experiments, significantly less than without the light filters. Of the samples that showed a significant indirect photolysis component, the level of nitrate measured in the samples was directly proportional to the observed enhancement ($k_{corrected}$ was normalized to the screening factor to correct for inner filter effects) (Figure 2.23) while the TOC was inversely related to the normalized $k_{corrected}$ (Figure 2.24). Thus, a clear inverse relationship existed between the TOC level and rate of photodegradation of the carbaryl. The trend is not at all surprising since NOM is an accepted HO* quencher. Likewise, a similar trend is observed for the total carbonate alkalinity, although the effect on the observed the rate coefficient
appears to be less sensitive to changes in alkalinity (Figure 2.24, inset). Corresponding to these trends, then, any differences observed in the corrected rate coefficients measured for the various sampling sites will result from the differences in the measured concentrations of NOM and carbonate species if the primary cause for the photoenhancement is due to the reaction of carbaryl with HO• generated from nitrate/nitrite photolysis. Thus, the measured degradation of carbaryl will decrease or increase in proportion to the nitrates and scavengers present. For four of the samples measured in this series of experiments, the data agreed with this hypothesis. Consequently, a major role of NOM and carbonate species are to inhibit the nitrate photolysis driven degradation reaction in this wetland water.

For experiments performed in the solar simulator, k_corrected was also correlated to the nitrate levels (Figure 2.21; 2.22) although it was not significantly correlated to TOC or carbonate levels (data not shown). One explanation for this trend is that under the full spectrum of sunlight, the NOM contributes to a degradation process which competes with its effect as a quencher. Such an interpretation, however, does not preclude that scavenging by carbonate and NOM will not be important. At the levels of carbonate species and TOC measured in the 6-29-98, 8-24-98, 9-8-98 OWC samples, the scavenging of HO• from the carbonate species would be expected to diminish as pH is reduced. Moreover, the scavenging effect of the carbonate species decreases when NOM levels are greater than 1 mg-C/L (Schwarzenbach et al., 1993). The level of NOM in these samples is comparatively high (all > 1 mg-C/L), and carbonate species are expected to play only a minor scavenging role at high pH and an insignificant role at low pH.
Attempting to correlate corrected rate coefficients to carbonate species resulted in no significant correlations at any pH. I calculated the percent contribution to the overall HO* scavenging of each species (based upon Equation 13-62 in Schwarzenbach et al., 1993) using the measured production rate HO* per mole nitrate for our lamp, and found that carbonate accounts for ~4% of the quenching, HCO3- accounts for ~29%, and NOM accounts for the dominant share (69-88%) of the overall scavenging at ambient pH. At lower pH, NOM scavenging dominates (> 99%) and carbonate species have little influence.

Preliminary calculations were performed to ascertain the observed light enhancement in the presence of nitrate. The xenon lamp used in this study was found to generate an intensity slightly greater than mid-summer sunlight in Columbus, OH (40° N) and the production rate of HO* from nitrate photolysis should be very similar to what is observed for what would be expected for sunlight near this latitude (3.0 × 10^13 M HO*/sec per μM nitrate) (Schwarzenbach et al., 1993). Indeed, the HO* production rate measured for our photoreactor was found to be 3.3 × 10^13 M HO*/sec per μM nitrate (White and Chin, unpublished data). Based upon this production rate and reported scavenging coefficients for the dominant natural water scavengers, I estimate the expected range of [HO*]_ss for these water samples at pH=4.3 to range from 4 × 10^17 to 3 × 10^15 M depending on the levels of nitrate and TOC in the system (Table 2.5). Indeed, a steady-state concentration on the order of 10^16 M HO* was produced in the low nitrate OWC.
water samples in our photoreactor system, comparable to my calculated values (White and Chin, unpublished data).

Carbaryl has been reported to react with HO\(^\cdot\) with a bimolecular rate constant of \(3.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}\) (Mabury and Crosby, 1996). Therefore, at my predicted \([\text{HO}^\cdot]\) concentrations for each water in the photoreactor, the reaction of carbaryl with HO\(^\cdot\) generated from NO\(_3^\cdot\) photolysis should account for < 1 to 25% of the indirect photolysis at pH = 4 (Table 2.5). These results are among the first (Wilson and Mabury, 2000) that demonstrate the efficacy of nitrates (i.e., unspiked solutions) in the indirect transformation of a pesticide in natural surface waters.

This result is less than the expected impact which, based upon a multiple regression calculation, predicted that nitrate/nitrite photolysis would promote up to 60% of the observed degradation. There are several possible explanations for this, including (1) error in the reported rate constant for the reaction of carbaryl, (2) the scavenging rate constant by NOM in OWC is in error and still lower than that reported in the literature, or, (3) the production rate used for these calculations is greater than the measured value. This raises an important point to consider. Recent literature (Zepp et al., 1987; Larson and Zepp, 1988; Brezonik and Fulkerson, 1998; Westerhoff et al., 1999) suggests that the scavenging coefficient for DOC is constant. Yet, if one uses the “average” reported value (\(2.5 \times 10^4 \text{ L/mgC/sec}\)) the nitrate induced effects become even less important. Using a lower than reported \(k_{DOC}\) results in greater contributions. These variations could result in 1-3 times difference in calculated half-lives for a contaminant of interest. This difference can be significant, especially in systems such as this wetland where water flows through
a basin. A difference in a half-life between 7 and 21 hours can mean a significant
difference in contaminant transformation before it is discharged into a receiving water.
Westerhoff et al. (1999) reported various k_{DOC}'s for different DOC's and correlates
reactivity to the origin of the NOM material. Therefore, differences in the reactivity of
the NOM may be important to consider when modeling contaminant fate in natural
waters.

The primary cause for depression of the indirect photolysis component in the
unaltered OWC samples (ambient pH around 8) is presumably due to a very efficient, pH
dependent direct photolysis which out-competes the indirect pathway for the low nitrate
waters at the higher pH. Additionally, the presence of bicarbonate and carbonate (present
in the water samples at 0.8 to 1.6 mM total CaCO$_3$ (Table 2.1)) will also diminish the
indirect nitrate mediated pathway although my scavenging predictions indicate that this
effect would be no more than 33% of the overall predicted rate coefficient at the lower
pH. The pH-adjusted samples were degassed and re-equilibrated with the atmosphere
prior to running the photolysis experiments, thus resulting in significant stripping of
inorganic carbonate species from the system.

Control photolysis experiments were performed to confirm the influence of nitrate
photochemistry on the photoinduced degradation of carbaryl. Photoreactions were
performed in phosphate buffered ([PO$_4^{3-}$]$_r$= 3.0 mM) MilliQ water (note: at this pH,
phosphate is not predicted to be an important quencher of HO* having a reported rate
constant of 1x10$^5$ M$^{-1}$sec$^{-1}$ (Buxton, 1988)) and OWC water at a pH (4.3) low enough to
quench the dark reaction pathway (Figure 2.22). In the “clean” (no NOM present)
experiments, the effect of adding 1.0 mM nitrate to the solution enhanced the photolytic reaction by a factor of 41 compared to the MilliQ control. Experiments with pH adjusted OWC water also showed that when the 8-24-98 RR sample, i.e., low nitrate sample, was "spiked" with NO$_3^-$ to levels observed in the 6-29-98 IN (1 mM), the indirect photolysis component increased by 216% to a level similar to that observed in the 6-29-98 IN sample (Figure 2.22). Zepp et al. (1987) showed that when the total scavenger concentration was constant for a given water sample, the rate coefficient measured for the nitrate-induced photooxidation of nitroanisole and nitrobenzene was directly proportional to the amount of nitrate added. Assuming a similar linear relationship exists in this experiment, I can attribute 54% of the overall observed rate coefficient to a nitrate promoted process by subtracting the $k_{\text{corrected}}$ (for dark reaction) of the reaction without the added nitrate from that measured for the reaction performed in the nitrate-spiked water. Predictions based upon the HO$^*$ production rate for this lamp, the levels of nitrate and TOC in this sample indicated that only 31% of the rate coefficient would be accounted for by nitrate promoted processes. Therefore, there is a 23% discrepancy and again, points to errors either in measurements of nitrate, TOC, and/or production-scavenging rates for this natural water. The 54% based upon the results is in agreement with what was expected based upon the multiple regression analysis.
Although nitrate photolysis could account for, at most, 25% of the transformation of carbaryl in the low pH samples (Table 2.5), the exact nature of the remaining contribution to the indirect photolysis was unknown. Multiple regression indicated that NOM also had an important promotion effect. In the low nitrate containing samples, up to 70% (in some cases, 9-8-98 OUT) of the carbaryl transformation could be attributed to NOM promoted reactions (Table 2.5). All the September and August water samples showed light-promoted degradation, even though the nitrate levels were very small (insignificant to produce large quantities of HO* (Figure 2.5; Table 2.5)). Even though there were two orders of magnitude less nitrate present in the September and August samples in comparison with the June samples, there was not a corresponding decrease in the measured photolysis rate (Figures 2.5; 2.21; 2.25; Table 2.2). These results suggest that NOM is an important photosensitizer as well as scavenger of reactive intermediates (like HO*) and photons (Hwang et al., 1987; Woodburn et al., 1993; Miller et al., 1980; Larson and Zepp, 1988) resulting in very low steady-state concentrations of reactive species in natural surface waters (Faust and Hoigne, 1987). Indeed, a correspondence was found between the corrected rate coefficients for carbaryl degradation and the level of TOC in the pH altered samples that did not contain high amounts of nitrate (August and September samples) (Figure 2.25). The role of NOM in facilitating the degradation of carbaryl in the OWC water did not corroborate the behavior reported for the influence of NOM on the degradation other phenyl N-methyl carbamates (Bachman and Patterson,
Thus, the scavenging and promoting activity of NOM may occur concurrently in natural waters and complicates the role that NOM plays in mediating photochemical reactions.

Reasons for the observed NOM photoenhancement could be due to several possibilities including: (1) a carbaryl excited-state reacting with ground-state NOM through electron transfer, (2) NOM triplet states reacting with ground state carbaryl through energy or electron transfer processes; (3) excited state NOM reacting with oxygen to form reactive oxygen species (e.g., \( \text{HO}^* \), \( \text{O}_2^* \), \( \text{O}_a\text{O} \)) that, in turn, react with carbaryl; (4) carbaryl forming charge transfer complexes with NOM; or (5) the interaction of metals (associated with organic ligands or free species in the water column) in promoting Fenton or photo-Fenton type chemistry.

The charge transfer (CT) idea has merit. Such an association could cause a red shift in absorption spectrum of carbaryl allowing for a lower energy (and more accessible) electronic transition. After excitation, electron transfer would be facilitated by the proximity of the donor (carbaryl) and acceptor (NOM) and result in the degradation of the carbaryl. Such a complex would explain observations of fluorescence quenching of carbaryl by DOC (Fang et al., 1998). Conversely, Wenska et al. (1997) found carbaryl formed very weak CT complexes in the ground state with nucleic acids. The fluorescence quenching by the formation of CT complexes (static quenching) was minimal in comparison to that occurring through dynamic processes. This finding could explain the results observed by Fang et al. (1998); however, since they did not measure lifetimes for their data, it is impossible to say whether dynamic or static processes are dominating the
observed quenching. At the magnitude of the association constant ($10^4$ L/kg) reported by Fang et al. (1998), if CT complexes were occurring between carbaryl and the NOM, I would expect approximately 30% of the carbaryl present to be associated with the natural organic matter. At this level, I should be able to observe CT complexes in the ground state spectrophotometrically.

I tested the CT complex theory by preparing solutions (in pH = 4.08, 5 mM phosphate buffer) of carbaryl ($2 \times 10^{-4}$ M) and carbaryl mixed with reconstituted OWC XAD-8 isolate (9.20 mg-C/L). No CT complexes were detectable (Figure 2.26), and the spectrum obtained from the mixture of carbaryl and the OWC XAD-8 equaled the sum of the individual spectra of carbaryl and the OWC XAD-8 obtained for the same concentrations. This test does not preclude the possibility that CT complexes do exist between carbaryl and NOM, but it does suggest that such an interaction is probably very weak and will not significantly influence a reaction between the two, thus, corroborating Wenska et al.'s findings.

While the possibility exists that charge transfer complexes may influence the reactivity of carbaryl with NOM, we doubt the interaction is hydrophobic in nature, i.e., the interaction associated with the partitioning behavior observed for contaminants. In recent literature, it has been reported that contaminants such as carbaryl "sorb" to NOM thus withdrawing them from the reactive solution. If hydrophobic interactions between natural organic matter and a contaminant were important in controlling the mechanism of reactivity for that contaminant, then comparing the reaction of carbaryl in a
predominantly hydrophobic versus hydrophilic NOM should help distinguish the importance of such a mechanism.

Isolating NOM according to its hydrophobic and hydrophilic properties has been performed now for many years. There are many methods that can accomplish such fractionation (Aiken, 1985) but one of the most prevalent is the use of nonionic, macroporous sorbents to retain natural organic matter through hydrophobic interactions (Aiken et al., 1992) from natural water samples as they are passed through a column packed with these resins (Aiken, 1985; Aiken et al., 1992). By aligning a series of columns packed with these resins, separation between the more hydrophobic and hydrophilic components of natural organic matter can be mostly achieved (Aiken et al., 1992). First, Amberlite XAD-8 (acrylic ester resin) is used to extract the more hydrophobic fraction of NOM in a natural water. After passing through the XAD-8 column, the effluent is passed through an XAD-4 column (styrene-divinylbenzene resin) to isolate the remaining hydrophilic acids that were not captured on the XAD-8. Prior to extraction, the humic acid fraction is separated from the fulvic by adjusting the pH of the natural water sample to 2. This results in the precipitation of the humic acid fraction (i.e., fulvic acid fraction remains dissolved). Since dissolved natural organic matter in natural waters is, in general, comprised of very little (10-15%) humic acid, the XAD extracts produce a "purified" sample of NOM that is fairly representative of the NOM in the natural water. The hydrophobic fulvic acid fraction is removed first by the XAD-8 column leaving behind the more hydrophilic acids that are then isolated by the XAD-4 column.
Hydrophilic acids separated via this technique were found to be lower in molecular weight, carbon and hydrogen contents, and aromatic carbon content, and higher in heteroaliphatic (i.e., carboxyl and ketone) carbon, oxygen and nitrogen contents than their hydrophobic XAD-8 counterparts (Aiken et al., 1992). The isolation of the OWC organic matter was performed, and carbaryl degradation reactions were carried in both XAD-8 and XAD-4 OWC dissolved NOM isolates. If hydrophobic interactions were important in influencing the reaction (i.e., that binding to organic matter decreased the observed degradation) then carbaryl should have a lower reactivity in the more hydrophobic fraction (XAD-8) than the hydrophilic fraction (XAD-4). The results, however, showed no such trend. The normalized (to the amount of organic material present in the solution) rate coefficients are practically indistinguishable, i.e., 1.4 ± 0.06 M⁻¹ min⁻¹ TOC for the XAD-8 compared to 1.3 ± 0.15 M⁻¹ min⁻¹ TOC for the XAD-4. Thus, the results from the degradation experiments with XAD-8 and XAD-4 extracts of OWC water yield data that counters the carbamate binding mechanism.

These results probably have more to do with the solubility of carbaryl than the nature of the organic material. Carbaryl's solubility is relatively high for an organic compound (40 mg/L @ 25°C) (MacKay et al., 1995), and thus, would be expected to have relatively low aqueous activity coefficient and organic carbon partitioning coefficient (K_{DOC}). Indeed, the literature reports that values of K_{DOC} measured using soil organic matter ranged from 229-575 L/kg (MacKay et al., 1995). Estimates based upon correlations from measured K_{OW} values yield predicted K_{DOC}'s in the same order of magnitude (~ 300-600 L/kg)(MacKay et al., 1995). K_{DOC}'s measured from substances
that more closely resemble aquatic DOM, i.e., algae and activated sludge, were even lower, ranging from 70-90 L/kg (Freitag et al., 1985). When the $K_{\text{DOC}}$ determined from the soil organic matter (375 L/kg) was used as an upper limit to estimate the extent of partitioning of carbaryl to the natural water organic matter, at most 0.4% of the carbaryl was predicted to be associated with the organic matter at the NOM level measured in the natural water samples. Thus, the effect should be indistinguishable from experimental error. While some have been attributing decreased photolysis rates in the presence of NOM to partitioning (Bachman and Patterson, 1999), such mechanisms make no sense in consideration of the reported solubility and $K_{\text{DOC}}$ for N-methyl-carbamates. In fact, the reported $K_{\text{DOC}}$'s for these substances are almost 100x's less than what Fang et al. (1998) reported for carbaryl based on fluorescence quenching technique. The decreased reactivity observed in these experiments may result from the unreactivity of their chosen DOC toward a sensitized mechanism at the pH of their experiments, and the inhibition of the direct photolysis due to inner filter effects (see above discussion of kinetics of those mechanisms).

The extent that inner filter effects will affect observed degradation rates becomes more important as the light approaches the cut-off wavelength for the photoreactor (290 nm). Since NOM absorbs more strongly in the lower wavelength regions, light screening would be expected to inhibit direct photolysis to a greater extent. Conversely, indirect photolytic processes resulting from absorption of light by natural water constituents would be expected to be promoted. The dominance of one type of photolysis mechanism over the other in controlling the degradation kinetics will be dependent on which
mechanism is more effective at transforming carbaryl. So at high pH's, if direct photolytic pathways predominate, then an increase of screening by the natural organic matter should inhibit the reaction; thus, $k_{obs}$ would be expected to be inversely proportional to the screening factor. Alternatively, at low pH's, where direct photolysis does not seem to be an important degradative mechanism, the screening factors should be directly proportionally to the observed degradation which can be interpreted to mean that NOM sensitized reactions occur significantly. These were the trends that were observed (Figure 2.27) although the correlations are poor. These observations contradict much of literature regarding carbamate phototransformation.

The above discussion has not addressed the idea that the observed reactivity could be due to a NOM component that is more reactive at a pH of 4 than 8. The discussion has focused on the idea that interaction of carbaryl with the NOM is not important in affecting the degradation rate of carbaryl. Yet, if the NOM sensitized reaction results from a bimolecular mechanism between the NOM and carbaryl, then interaction of carbaryl with the NOM should be important. Since the pH of a solution affects the structure of NOM, this may consequently affect its interaction with carbaryl. The deprotonation of NOM at higher pH's causes it to become more polar, alters its structure (charge repulsion), and decreases its ability to "bind" hydrophobic compounds (Schlautman and Morgan, 1993). If $\pi$-interactions are necessary to bring about the orbital overlap necessary for both inner- and outer- electron transfer reaction (Hubig et al., 1999), then association with organic matter will be very important. Likewise, a higher ionic strength, will significantly affect the structure of the NOM while not
affecting the solubility of soluble compounds to a great extent. A higher ionic strength will cause NOM to be compressed through electrostriction, resulting in an NOM with less “voids”, *i.e.* areas for interaction with organic compounds.

On the basis of this theory, I would expect the NOM to be more reactive at a lower pH and at lower ionic strengths. The data provides no evidence of NOM sensitization at the higher pH's, which at first glance seems consistent with the above interpretation (*i.e.*, that interactions with NOM is governing the photosensitization by NOM). Following this reasoning, one would expect that the hydrophobic or hydrophilic character of the NOM should influence reactivity. Since it does not (as evidenced from the XAD8/4 reactions), one must conclude that interaction with NOM is not the causative agent for the observed reaction.

Furthermore, if the changes in the photochemical reactivity of the NOM at the two pHs were due to changes in the light absorption properties of the NOM (and generation of reactive NOM triplet states), the UV/VIS spectra of the NOM should show certain shifts in the spectra between the two pH's. The UV/VIS spectra taken at both pH's, however, show little difference (Figures A.3-10) and therefore, observed reactivity must not be due to pH-induced changes in the chromophores of the NOM.

Therefore, the observed promotion in the degradation of carbaryl by NOM at low pH results from metal mediation and/or the photoproduction of ROS. An argument can be made that trace metals, free and associated with organic matter, could be the primary photoreactive reagents present in solution. The observed pH dependency is consistent with the literature in which numerous photochemical processes that were promoted by
free and/or complexed iron showed similar pH trends (Balmer and Sulzberger, 1999; Pignatello, 1992; Emmenegger et al., 1998; Miles and Brezonik, 1981; Voelker et al., 1997). In order to test the role of iron or other trace metals in these reactions, the most reactive water, the June Inlet water, was passed through a column packed with a cation-exchange resin (proton saturated) which should remove any free or weakly complexed (labile) metals from the water sample. The effluent was collected and the pH of the effluent was raised back to 4.35. While some of the NOM would be retained on the resin resulting in a loss of NOM from the solution, the level of nitrate should remain close to the original sample. Indeed, TOC analysis of the effluent indicated that approximately 16% of the NOM was lost through this process. UV/VIS indicated that no loss of nitrate occurred (i.e., little difference in the nitrate region of the UV/VIS spectrum when compared with that from pH adjusted June Inlet sample). In the case that free or labile metals were responsible for the observed reaction in the original sample, the removal of these species from the water should result in sample that would exhibit decreased reactivity in the photodegradation of carbaryl. When the experiment was performed, the $k_{\text{obs}}$ was $0.00279 \text{ min}^{-1}$, or, 4% higher than that observed for the pH adjusted June Inlet sample (Figure 2.22). When $k_{\text{obs}}$ is normalized to the TOC, the photoenhancement in the H+ water is 24% higher than that in the June inlet sample. This result is what I would expect if the nitrate and NOM were primarily responsible for the photoenhancement: the loss of NOM in the cation exchange process should result in an effluent that contains less hydroxyl radical scavengers and chromophores (which contribute to light screening), and an elevated rate coefficient should be observed. Since, NOM acts as a photosensitizer,
the extent of the elevation of the rate coefficient will be reduced because the pool of NOM photosensitizers available for reaction would have been also reduced.

Furthermore, the control experiments with XAD-8/4 OWC isolates showed the same level of photoenhancement as samples containing low total nitrates. The low pH (2) used during the NOM extraction protocol also releases a large percentage of metals bound in the organic material. These metals will be minimally retained on the non-ionic resin in the low pH water and will pass through the columns in the effluent; however, as an additional precaution from metal contamination, XAD-8/4 eluates are passed through a proton-saturated, cation exchange column after the XAD extraction before lyophilization (Aiken, 1985; Aiken et al., 1992). This procedure ensures that bound metal content of the NOM is minimized (it does not preclude the possibility that metals may be incorporated within the NOM matrix). Still, these XAD-8/4 isolates sensitized the degradation of carbaryl at similar levels as the raw, low nitrate-containing water samples (Figure 2.22; 2.25).

While no strong conclusions can be made about the role of the strongly bound fraction of metals, the results from the cation exchanged water sample and XAD-8/4 studies suggest that free and labile metals play little role in mediating these reactions. The role of stray metal complexes will be discussed in subsequent chapters.
2.4 Conclusions

As expected, the photodegradation of carbaryl was greatly enhanced by irradiation in the solar simulator in comparison with the degradation measured for monochromatic light (366 nm). Indirect photolytic pathways influenced the photodegradation of carbaryl in a natural wetland surface water. The enhancement by light appears to be related to the concentration of NOM and nitrates, the alkalinity, and the pH. No evidence was found to support the idea that free or labile metals promoted indirect processes.

To the best of my knowledge this study is the first to observe indirect photolytic degradation of a contaminant by naturally occurring nitrate levels in a wetland water. The results suggest that nitrates may play an important part in the indirect photolysis of non-point source pollutants passing through OWC during certain times of the year. The amount of nitrates and nitrites present in wetlands such as OWC will be largely dependent upon the amount of agricultural runoff and municipal inputs into the system and the degree of cycling that occurs by phytoplankton, microorganisms, and higher plants. Conceivably, nitrates in certain wetlands could be sufficiently high enough to impact contaminant photolysis if other scavengers such as carbonates and NOM concentrations are relatively small (e.g., cranberry bogs in the Northeast).

It was also interesting to see how some constituents behaved in dual roles. For example, natural organic matter, while inhibiting the photochemical degradation pathway of nitrate, promoted another light induced degradation pathway for carbaryl. In addition, while the carbonate alkalinity inhibited carbaryl's degradation through the scavenging of
reactive intermediates, it enhanced the direct photolytic degradation through buffering the pH.

The results from the direct photolysis work may have important implications for the photodegradation of other N-methyl carbamates in natural systems. A pH dependent direct photolysis indicates that the pH of the natural water may in some circumstances control the extent of photolysis of these types of contaminants. Thus, caution must be used when predicting direct photolysis rates based upon natural water attenuation, the absorption spectrum of the contaminant, and available light as is common practice (e.g., GCSolar calculations). If we are to develop reliable models to understand the fate of contaminants in aqueous environments, it is important to consider how natural water constituents affect the direct as well as indirect mechanisms. The finding that carbaryl’s photodegradation is promoted at a high pH is extremely significant for this region because many of Ohio’s waters are alkaline, and therefore, carbaryl would be expected to be less stable than what has been reported for this compound (Wolfe et al., 1978).

Finally, the data presented here was inconclusive concerning the role that metals associated with organic matter may have influencing the reaction and represents an important venue of research that needs further investigation. To a limited extent, this topic was researched in the next chapter. Future research must also include the positive identification of the other daughter species besides 1-naphthol. Identification and quantification of daughter species should help to elucidate the pathways of the different light promoted mechanisms.
<table>
<thead>
<tr>
<th>Sample</th>
<th>pH(^1)</th>
<th>TOC (mg/L)</th>
<th>(\varepsilon)@280nm(^3) (M(^-1)cm(^{-1}))</th>
<th>(S_x)^4 (at 290-370 nm)</th>
<th>Specific Conductivity ((\mu S/cm))</th>
<th>Alkalinity (mg/L CaCO(_3))</th>
<th>Nitrate (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inlet</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>June</td>
<td>7.65</td>
<td>7.15 (0.87)</td>
<td>307</td>
<td>0.874</td>
<td>425</td>
<td>83.9</td>
<td>1.01</td>
</tr>
<tr>
<td>September</td>
<td>7.78</td>
<td>5.24 (0.40)</td>
<td>242</td>
<td>0.940</td>
<td>540</td>
<td>155.1</td>
<td>0.0274</td>
</tr>
<tr>
<td><strong>Railroad</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>June</td>
<td>NA(^2)</td>
<td>7.06 (1.07)</td>
<td>333</td>
<td>0.841</td>
<td>NA(^2)</td>
<td>NA(^2)</td>
<td>0.790</td>
</tr>
<tr>
<td>August</td>
<td>7.71</td>
<td>6.70 (1.44)</td>
<td>219</td>
<td>0.917</td>
<td>437</td>
<td>155.2</td>
<td>0.0131</td>
</tr>
<tr>
<td>September</td>
<td>7.80</td>
<td>6.42 (0.87)</td>
<td>288</td>
<td>0.914</td>
<td>411</td>
<td>134.4</td>
<td>0.0295</td>
</tr>
<tr>
<td><strong>Outlet</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>June</td>
<td>8.09</td>
<td>6.17 (3.72)</td>
<td>242</td>
<td>0.931</td>
<td>396</td>
<td>118.3</td>
<td>0.154</td>
</tr>
<tr>
<td>September</td>
<td>7.96</td>
<td>2.17 (0.94)</td>
<td>166</td>
<td>0.980</td>
<td>274</td>
<td>89.2</td>
<td>0.0185</td>
</tr>
</tbody>
</table>

\(^1\) pH Measured at field site. \(^2\) Data not available. \(^3\) \(\varepsilon\) = calculated molar absorptivity for various OWC waters (corrected for nitrate absorption). \(^4\) The calculated overall screening factor, \(S_x\). The screening factor is used to quantify the effect of light attenuation by natural waters on the direct photolysis rate. The wavelength specific light screening factor, \(S_x\), can be calculated from \(S_x = 1 - 10^{-\varepsilon I}\) where \(I\) is the pathlength of the test tubes used for the experiments and \(\alpha\) is the attenuation coefficient (simply the measured absorbance for a given wavelength when the cuvette pathlength is 1 cm). \(S_x\) here was calculated for \(\lambda = 290-370\) nm.

Table 2.1: Water quality characteristics for water samples taken from Old Woman Creek (OWC) in June, August, and September of 1998. Values in parenthesis represent %CV for replicate samples.
<table>
<thead>
<tr>
<th>Description</th>
<th>pH ±</th>
<th>k&lt;sub&gt;min&lt;/sub&gt; (min&lt;sup&gt;-1&lt;/sup&gt;) ±10&lt;sup&gt;-4&lt;/sup&gt;</th>
<th>Dark</th>
<th>% Mass Balance</th>
<th>Light</th>
<th>% Mass Balance</th>
<th>k&lt;sub&gt;Direct&lt;/sub&gt;</th>
<th>Corrected ±10&lt;sup&gt;-4&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inlet</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>June</td>
<td>4.37</td>
<td>0.0435 ± 0.0262</td>
<td>98</td>
<td>2.73 ± 0.05</td>
<td>25</td>
<td>0.12</td>
<td>2.69 ± 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.86</td>
<td>2.97 ± 0.15</td>
<td>96</td>
<td>4.56 ± 0.17</td>
<td>24</td>
<td>1.5</td>
<td>1.59 ± 0.23</td>
<td></td>
</tr>
<tr>
<td>September</td>
<td>4.32</td>
<td>0.115 ± 0.047</td>
<td>95</td>
<td>0.86 ± 0.05</td>
<td>64</td>
<td>0.13</td>
<td>0.744 ± 0.070</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.85</td>
<td>2.40 ± 0.11</td>
<td>94</td>
<td>3.28 ± 0.11</td>
<td>34</td>
<td>1.6</td>
<td>0.876 ± 0.149</td>
<td></td>
</tr>
<tr>
<td><strong>Railroad</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>June</td>
<td>4.38</td>
<td>0.136 ± 0.053</td>
<td>93</td>
<td>2.32 ± 0.08</td>
<td>33</td>
<td>0.12</td>
<td>2.18 ± 0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.93</td>
<td>2.71 ± 0.16</td>
<td>98</td>
<td>4.46 ± 0.19</td>
<td>20</td>
<td>1.7</td>
<td>1.75 ± 0.25</td>
<td></td>
</tr>
<tr>
<td>August</td>
<td>4.37</td>
<td>0.0342 ± 0.0273</td>
<td>99</td>
<td>1.10 ± 0.03</td>
<td>58</td>
<td>0.13</td>
<td>1.06 ± 0.04</td>
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</tr>
<tr>
<td></td>
<td>7.96</td>
<td>1.73 ± 0.08</td>
<td>94</td>
<td>3.75 ± 0.10</td>
<td>25</td>
<td>2.0</td>
<td>2.02 ± 0.13</td>
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</tr>
<tr>
<td>September</td>
<td>4.31</td>
<td>0.13 ± 0.08</td>
<td>94</td>
<td>1.25 ± 0.09</td>
<td>50</td>
<td>0.13</td>
<td>1.12 ± 0.12</td>
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</tr>
<tr>
<td></td>
<td>8.02</td>
<td>3.36 ± 0.13</td>
<td>92</td>
<td>4.95 ± 0.15</td>
<td>20</td>
<td>2.3</td>
<td>1.59 ± 0.12</td>
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<tr>
<td><strong>Outlet</strong></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>June</td>
<td>4.34</td>
<td>0.12 ± 0.05</td>
<td>94</td>
<td>1.37 ± 0.06</td>
<td>50</td>
<td>0.13</td>
<td>1.25 ± 0.08</td>
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<tr>
<td></td>
<td>8.2</td>
<td>4.32 ± 0.31</td>
<td>98</td>
<td>6.73 ± 0.28</td>
<td>9</td>
<td>2.4</td>
<td>2.41 ± 0.42</td>
<td></td>
</tr>
<tr>
<td>September</td>
<td>4.31</td>
<td>0.0501 ± 0.0226</td>
<td>97</td>
<td>0.48 ± 0.021</td>
<td>75</td>
<td>0.14</td>
<td>0.426 ± 0.031</td>
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<tr>
<td></td>
<td>7.76</td>
<td>1.94 ± 0.13</td>
<td>96</td>
<td>3.10 ± 0.133</td>
<td>39</td>
<td>1.14</td>
<td>1.16 ± 0.19</td>
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</tr>
<tr>
<td><strong>Buffered MilliQ Water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>4.35</td>
<td>0.116 ± 0.048</td>
<td>90</td>
<td>0.236 ± 0.04</td>
<td>87</td>
<td>0.14</td>
<td>0.119 ± 0.063</td>
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<tr>
<td>Borate</td>
<td>7.99</td>
<td>2.16 ± 0.13</td>
<td>92</td>
<td>4.32 ± 0.14</td>
<td>20</td>
<td>2.3</td>
<td>2.16 ± 0.19</td>
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</tr>
</tbody>
</table>

<sup>1</sup>Values are the average pH.  <sup>2</sup>Values ± are the 95% confidence level.  <sup>3</sup>Calculated as the sum of all quantifiable species measured at the end of the time course divided by initial carbaryl concentration.  <sup>4</sup>Values predicted from S<sub>x</sub> × k<sub>direct</sub> (predicted from linear regression of measured k<sub>direct</sub> vs [OH-]).  <sup>5</sup>Rate constants were corrected for the dark reactions. Values in parenthesis are one standard deviation.

Table 2.2: Measured initial rate coefficients and total mass balances for the degradation of carbaryl in Old Woman Creek wetland water in the dark and light.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temp (K)</th>
<th>$\lambda_{exc}$(nm)</th>
<th>$\varepsilon$(M$^{-1}$cm$^{-1}$)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\Phi_T$</th>
<th>$\tau$ (ns)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% (v/v) MeOH</td>
<td>281</td>
<td></td>
<td>328</td>
<td>0.146</td>
<td></td>
<td></td>
<td>Larkin and Day, 1979</td>
</tr>
<tr>
<td>Ethanol</td>
<td>298</td>
<td>281</td>
<td>325</td>
<td>0.11</td>
<td>32.8</td>
<td></td>
<td>Semeluk et al., 1978</td>
</tr>
<tr>
<td>Ethanol</td>
<td>77</td>
<td>273.2 283.1</td>
<td>315.7</td>
<td></td>
<td></td>
<td></td>
<td>Files and Winefordner, 1987</td>
</tr>
<tr>
<td></td>
<td></td>
<td>294.3</td>
<td>320.7</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>330.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>335.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Ethanol</td>
<td>285 (279)</td>
<td></td>
<td>333</td>
<td></td>
<td></td>
<td></td>
<td>Blanco and Sanchez, 1988</td>
</tr>
<tr>
<td>Water</td>
<td>282</td>
<td></td>
<td>330; 660</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPA (5:5:2)$^1$</td>
<td>293</td>
<td>262 (290)$^2$</td>
<td>340.1</td>
<td></td>
<td></td>
<td></td>
<td>Addison et al., 1977</td>
</tr>
<tr>
<td>EPA (5:5:2)$^1$</td>
<td>293</td>
<td>262 (290)$^2$</td>
<td>(326, 503$^*$)</td>
<td></td>
<td></td>
<td></td>
<td>Addison et al., 1977</td>
</tr>
<tr>
<td>Water</td>
<td>293</td>
<td>278.5 5800</td>
<td>334</td>
<td>0.21, 0.23</td>
<td>29.0, 30.1</td>
<td></td>
<td>Wenska, 1997</td>
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<tr>
<td>MeOH</td>
<td>&quot;</td>
<td>279 6400</td>
<td>335</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-propanol</td>
<td>&quot;</td>
<td>279.5 6100</td>
<td>334</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>&quot;</td>
<td>282.5 6400</td>
<td>336</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>&quot;</td>
<td>279.5 6200</td>
<td>334</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeCl$_2$</td>
<td>&quot;</td>
<td>280.5 6200</td>
<td>336</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$EPA is a mixture of ether, isopentane, ethanol in a ratio of 5:5:2, respectively. $^*$ with phosphorescope; $^2$ values in parenthesis indicate UV/VIS absorbance data.

Table 2.3: Measured fluorescence of phosphorescence data reported for carbaryl in a number of solvents.
Table 2.4: Fluorescence (singlet-state) lifetimes of carbaryl and 1-naphthol measured by TCSPC in buffered aqueous solutions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aqueous Conditions</th>
<th>$\tau$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbaryl</td>
<td>pH = 4.33$^1$</td>
<td>31.583</td>
</tr>
<tr>
<td>$\lambda_{\text{exit}}$ = 290 nm</td>
<td>pH = 9.04$^1$</td>
<td>31.874</td>
</tr>
<tr>
<td>$\lambda_{\text{emit}}$ = 335 nm</td>
<td>pH = 10.0 (NaOH)</td>
<td>32.070</td>
</tr>
<tr>
<td>1-Naphthol</td>
<td>pH = 4.33$^1$</td>
<td>~7.8</td>
</tr>
<tr>
<td>$\lambda_{\text{exit}}$ = 290 nm</td>
<td>pH = 9.04$^1$</td>
<td>~7.8</td>
</tr>
<tr>
<td>$\lambda_{\text{emit}}$ = 467 nm</td>
<td>MilliQ (no buffer)</td>
<td>~7.8</td>
</tr>
</tbody>
</table>

$^1$Phosphate buffer (5 mM) was used to stabilize pH. Solutions (0.01 M) of HCl and NaOH were used to adjust pH to desired value.
<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>TOC (mg/L)</th>
<th>Nitrate (mM)</th>
<th>Alkalinity (mg/L CaCO₃)</th>
<th>[HO⁻]ₙₙ</th>
<th>kₚₑₙ (min⁻¹)</th>
<th>% kₚₑₙ of kₙₑₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>June</td>
<td>4.37</td>
<td>7.15 (0.87)</td>
<td>1.01</td>
<td>83.9</td>
<td>3.3×10⁻¹⁵</td>
<td>6.8×10⁻⁴</td>
<td>25</td>
</tr>
<tr>
<td>September</td>
<td>4.32</td>
<td>5.24 (0.40)</td>
<td>0.0274</td>
<td>155.1</td>
<td>1.2×10⁻¹⁶</td>
<td>2.5×10⁻⁵</td>
<td>3.4</td>
</tr>
<tr>
<td>Railroad</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>June</td>
<td>NA²</td>
<td>7.06 (1.07)</td>
<td>0.790</td>
<td>NA²</td>
<td>2.6×10⁻¹⁵</td>
<td>5.4×10⁻⁴</td>
<td>25</td>
</tr>
<tr>
<td>August</td>
<td>4.37</td>
<td>6.70 (1.44)</td>
<td>0.0131</td>
<td>155.2</td>
<td>4.6×10⁻¹⁷</td>
<td>9.4×10⁻⁶</td>
<td>0.90</td>
</tr>
<tr>
<td>September</td>
<td>4.31</td>
<td>6.42 (0.87)</td>
<td>0.0295</td>
<td>134.4</td>
<td>1.1×10⁻¹⁶</td>
<td>2.2×10⁻⁵</td>
<td>2.0</td>
</tr>
<tr>
<td>Outlet</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>June</td>
<td>4.34</td>
<td>6.17 (3.72)</td>
<td>0.154</td>
<td>118.3</td>
<td>5.9×10⁻¹⁶</td>
<td>1.2×10⁻⁴</td>
<td>10</td>
</tr>
<tr>
<td>September</td>
<td>4.31</td>
<td>2.17 (0.94)</td>
<td>0.0185</td>
<td>89.2</td>
<td>2.0×10⁻¹⁶</td>
<td>4.1×10⁻⁵</td>
<td>9.5</td>
</tr>
</tbody>
</table>

¹average pH measured in samples. ²Data not available

Table 2.5: Predicted [HO⁻]ₙₙ for water samples taken from Old Woman Creek (OWC) in June, August, and September of 1998 in the pH adjusted water.
Figure 2.1: Map of Old Woman Creek Estuarine Reserve (OWC), Huron, OH. Water samples were obtained from the Inlet (IN), Railroad (RR), and Outlet (OUT).
Figure 2.2: Spatial and temporal variability in the molar absorptivity ($\varepsilon$) at $\lambda = 280$ nm (A), nitrate concentration (B), and total iron level (C) measured in the OWC wetland water samples during the 1998 field season.
Figure 2.3: Variation of screening factor with wavelength for wetland water samples.

Figure 2.4: Photoinduced degradation of carbaryl in OWC wetland water samples at their natural pH (~8). Error bars represent the 95% CI.
Figure 2.5: Photoinduced degradation of carbaryl in pH adjusted (~4) water samples. Error bars represent the 95% CI.

Figure 2.6: Photoinduced degradation of carbaryl in OWC water sampled from the Inlet site on June 29, 1998 at ambient pH (~8).
Figure 2.7: Photoinduced degradation of carbaryl in the OWC 6-29-98 Inlet water in pH adjusted (4.37) water samples.

Figure 2.8: A comparison of the corrected (for dark reaction) rate coefficients for the photoinduced degradation of carbaryl in altered (pH 4) and unaltered (pH 8) OWC samples. Error bars represent the propagated error (one standard deviation).
Figure 2.9: Base-catalyzed elimination pathway for the N-methyl carbamate, carbaryl.
Figure 2.10: Carbaryl UV/VIS absorption spectra as a function of pH.

Figure 2.11: Change in UV/VIS absorption spectrum of carbaryl (pH = 9.04) with time.
Figure 2.12: Dependency of the direct photolysis rate coefficient, \( k_{\text{obs}} \) (hr\(^{-1}\)), for carbaryl degradation on the pH ([OH\(^-\)]). Dotted lines represent the 95% CI.

\[
k_{\text{obs}} = 2.95 \times 10^4 \times ([OH^-]) + 1.00 \times 10^{-3}
\]
\[R^2 = 0.998\]

Figure 2.13: Dependency of correct (for dark reaction) rate coefficient and quantum yield for the direct photolysis of carbaryl at \( \lambda = 366 \) nm. Dotted lines represent the 95% CI.

\[
k_{\text{correct}} = 1.05 \times 10^4 \times ([OH^-]) + 9.94 \times 10^{-4}
\]
\[R^2 = 0.987\]

\[
k_{\text{correct}} = 3.83 \times 10^2 \times ([OH^-]) + 3.83 \times 10^{-4}
\]
\[R^2 = 0.987\]
Figure 2.14: Effect of 1-naphthol on the photoinduced degradation of carbaryl. 1-Naphthol added at the various mole ratios given in the legend.
Figure 2.15: Fluorescence lifetime measurements for carbaryl using TCSPC.

Figure 2.16: Fluorescence lifetime measurements for 1-naphthol using TCSPC.
Figure 2.17: Direct photolysis of carbaryl in high pH (8.00) solutions with and without argon sparging.
Figure 2.18: The contribution that direct and indirect photolysis have to $k_{\text{corrected}}$ for carbaryl degradation in tested wetland waters. Error bars represent the propagated error (one standard deviation).

Figure 2.19: The contribution that direct and indirect photolysis have to $k_{\text{corrected}}$ for carbaryl degradation in the pH adjusted waters. Error bars represent the propagated error (one standard deviation).
Figure 2.20: Multiple regression analysis of $k_{abs}$ (min$^{-1}$) for carbaryl photodegradation versus the [DOC] (mg-C/L) and [Nitrate] (M).
Figure 2.21: Correlation between nitrate level with pseudo-first order rate coefficient (corrected for the dark reaction and normalized to the TOC) for the samples run in pH adjusted (~4) OWC wetland water and control solutions.
Figure 2.22: Correspondence of nitrate level to the corrected (for the dark reaction) rate coefficient for carbaryl degradation. Plot shows the spatial and temporal trends of nitrate levels. Error bars represent the propagated error (95% CI).
Figure 2.23: Positive correlation observed between the nitrate level and the rate coefficient ($k_{\text{corrected}}$; corrected for the dark reaction) measured for the photodegradation (at $\lambda = 366$ nm) of carbaryl. Each $k_{\text{corrected}}$ was normalized to the screening factor determined for a given OWC water sample to correct for differences due to inner filter effects. Error bars represent the propagated error (one standard deviation).

Figure 2.24: Inverse correlations observed between NOM (measured as the TOC) and alkalinity (inset) and the rate coefficient ($k_{\text{corrected}}$; corrected for the dark reaction) measured for the photodegradation (at $\lambda = 366$ nm) of carbaryl. Each $k_{\text{corrected}}$ was normalized to the screening factor determined for a given OWC water sample to correct for differences due to inner filter effects. Error bars represent the propagated error (one standard deviation).
Figure 2.25: Comparison of corrected (for the dark reaction) rate coefficients determined for the photoinduced degradation of carbaryl in low nitrate (<50 mM) OWC samples. Hydrophobic and hydrophilic samples were obtained by dissolving XAD-8 and -4 isolates in buffered MilliQ water. Error bars represent the propagated error (95%CI).
Figure 2.26: UV/VIS spectra providing evidence that carbaryl does not form charge transfer complexes with the NOM to a significant extent.
Figure 2.27: Relationship between the light screening factor measured at $\lambda = 290 \text{ nm}$ and corrected (for the dark reaction) rate coefficients for carbaryl degradation at pHs of 8 (A) and 4 (B).
CHAPTER 3

EFFECT OF WETLAND WATER CONSTITUENTS ON THE PHOTINDUCED DEGRADATION OF THE HERBICIDE ALACHLOR

3.1 Introduction

Non-point source pollution from surface runoff contaminated with agrochemicals threatens communities that rely on surface water for their drinking water supply and recreation (Richards and Baker, 1993). Photolysis is an important degradative pathway for many agrochemicals (Kolpin and Kalkhoff, 1993; Mabury and Crosby, 1994) and can occur through direct and indirect pathways. Total nitrates (nitrate + nitrite) are pertinent nutrients that have been well studied with respect to their photochemistry and are widely recognized as generators of the highly reactive hydroxyl radical (Zepp et al., 1987) and can promote contaminant destruction. While nitrate levels are typically low in many natural waters (< 10 μM), they are often elevated in wetlands receiving agricultural runoff after precipitation events (Zepp et al., 1987). Moreover, wetlands, in comparison to other water bodies, are rich in natural organic matter (NOM), capable of absorbing sunlight and catalyzing the transformation of organic compounds via additional indirect pathways.
(Blough and Zepp, 1995). Furthermore, metals are ubiquitous in all natural waters. While the ability of trace metals to catalyze the generation of reactive transients in natural waters in the light is well known (Voelker et al., 1997), little attention has been given to assessing whether the photoreactivity of metals at their ambient levels in natural waters will promote the degradation of recalcitrant contaminants. Thus, indirect photolysis arising from a number of pathways may be an important in degrading non-chromophoric organic contaminants in these wetland systems.

Therefore, this study is targeted to provide an understanding of the indirect photochemical processes occurring in a wetland surface waters. In order to evaluate the significance of these processes, the degradation of a photochemically recalcitrant, non-point source pollutant was studied. Alachlor was chosen as the probe molecule because of its ubiquitous use in Ohio agriculture and its environmental persistence (Kolpin et al., 1996).

3.1.1 Environmental Fate of Alachlor

Alachlor (2-chloro-2',6'-diethyl-N-(methoxymethyl)-acetanilide) is a pre-emergent herbicide used to control grass and broadleaf weeds in corn and soybean crops (Kolpin et al., 1996). As a member of the chloroacetanilide family, its structure contains an aromatic ring, amide, and ether functional groups (Figure 3.1). Alachlor is a probable human carcinogen (Novak et al., 1997) and the maximum contaminant level (MCL) set for drinking water is 2 μg L⁻¹ (Kolpin et al., 1996). Alachlor is fairly recalcitrant in the
aqueous environment, having a measured half-life of 23 days in river water (MacKay et al., 1995). Because it has a high aqueous solubility (~242 mg/L) (MacKay et al., 1995), one primary environmental concern is that its widespread use will lead to non-point source contamination (Loch, 1999). Indeed, chloroacetanilides and their derivative have been detected in many surface waters (Galassi et al., 1996), near-surface aquifers (Kolpin et al., 1996), and groundwaters (Kolpin et al., 1998), often at levels approximating their MCLs (Wilson and Mabury, 2000).

A primary mode of degradation is through biotransformation. Resistant plants and microorganisms detoxify their systems by inducing the reaction of glutathione or homoglutathione with the chloroacetyl sidechain (Thurman et al., 1996; Leavitt and Penner, 1979). Thiols such as glutathione transform chloroacetanilides via nucleophilic attack, resulting in dechlorination and the formation of the gluathione-acetanilide conjugate. These conjugates eventually degrade into the sulfonic acid (ESA), oxanillic acid, and sulfinylacetic acid derivatives of alachlor (Graham et al., 1999) which account for the major percentage of the alachlor dispersed in the environment.

Alachlor can react abiotically, however, quite readily under anaerobic conditions. Under sulfate reducing conditions, it is susceptible to both nucleophilic substitution and reduction from reduced sulfate species (e.g., $S^{2-}$, $HS^-$) (Stamper et al, 1997; Novak et al., 1997; Loch, 1999). The mechanism for the reaction is attributed to either the nucleophilic attack of the reduced sulfide species on the carbon bonded to the chlorine or to reductive dehalogenation. Half-lives measured for these reactions were as small as a few hours at high, but environmentally relevant, total sulfur concentrations (Loch, 1999).
In contrast, alachlor does not react appreciably through abiotic mechanisms in dark, aerobic aqueous environments. It has been reported to have a high hydrolysis half-life (> 365 days in clean, alkaline systems) (Mackay et al., 1995). Therefore, photolysis is one of the few pathways that result in the transformation of alachlor under aerobic conditions (Wilson and Mabury, 2000).

The mechanism for direct photolysis of alachlor is thought to proceed via the following reaction mechanism (Figure 3.1). The products of the direct photolysis are primarily the dechlorinated alachlor species (hydroxyalachlor and 2',6'-diethyl-N-methylacetanilide) and the lactam species, 8-ethyl-1-methoxy-methyl-4-methyl-2-oxo-1,2,3,4-tetraquinoline (Penuela and Barcelo, 1996; Schmidt et al., 1995). The half-life for alachlor measured in deionized water under solar irradiation was very slow; exposure for over five days produced little degradation (Penuela and Barcelo, 1996). In comparison, biotransformation processes have measured half-lives in the range of ~15-20 days depending on the aquatic system (Graham et al., 1999; Chiron et al., 1995; Mackay et al., 1995).

Although alachlor has been reported to have little direct photolytic reactivity, it is susceptible to indirect (through its reaction with HO•) photolysis (Mabury and Crosby, 1996). The photo-Fenton reaction, used in the water treatment field as an advanced oxidation process (AOP), was very efficient in degrading alachlor (Huston and Pignatello, 1999). In less than 30 minutes of irradiation with a fluorescent blacklight (UV source in the range of λ from 300-400 nm), alachlor was completely transformed with considerable mineralization within 120 minutes. The principle oxidant in this system is the hydroxyl
radical whose production is promoted catalytically by the addition of iron to a solution of 
H_2O_2 according to the following equations:

\[ Fe^{2+} + H_2O_2 \longrightarrow Fe(OH)^{2+} + HO\cdot \]  
\[ Fe(OH)^{2+} \text{ or } Fe(OH)_2^+ \longrightarrow Fe^{2+} + HO\cdot \]  

In “clean” solutions, i.e., the absence of ligands other than OH^-, the photo-Fenton reaction is optimum at a pH of 2.8 (Pignatello, 1992) where Fe(III) is equally distributed as the Fe^{3+} ion and the photoreactive Fe(OH)^{2+} (Huston and Pignatello, 1999).

Photocatalytic oxidation of alachlor can also be achieved using the semiconductor oxide, TiO_2 (Penuela and Barcelo, 1996). In these systems, alachlor degradation occurs quite readily since systems are spiked with high levels (> 0.01 M H_2O_2 and 50 µM Fe^{3+}). It is not clear, however, if these reactions will be efficient in aqueous systems such as natural waters, where the levels of dissolved iron and hydrogen peroxide can be orders of magnitude lower. Moreover, most the Fe^{3+} will exist as organo-complexes whose effect in promoting contaminant degradation is unknown. These questions were investigated in the current study.

Alachlor can also be photodegraded in several types of freshwaters (Chiron et al., 1995). In one experiment, the photoinduced degradation of alachlor was promoted by 66% when irradiated in a buffered (pH 6.8) river water (TOC 4 mg/L) in comparison to the reaction performed in buffered distilled water (Chiron et al., 1995; Barcelo et al., 1995). The extent of the photodegradation was found to depend on water type, humic substances, pH, and ionic strength. For the pH effect, alachlor was found to degrade to a
lesser extent at a higher pH (~ 7). This behavior was attributed to a change in the efficiency of alachlor partitioning to the NOM phase between low and high pH samples (Chiron et al., 1995). It was suggested that at a higher pH, more alachlor would partition to the NOM an interaction which would remove alachlor from the reactive matrix, i.e., bulk solution. Therefore, it was hypothesized that alachlor is degraded to a lesser extent at a higher pH because less was present in the bulk solution with the reactive species. These studies are important because they showed that alachlor degradation could be promoted by the presence of humic materials, though no mechanistic interpretation was offered.

3.1.2 Goals for this Study

This research seeks to evaluate the importance that photolytic mechanisms will have on the fate of alachlor in natural wetland waters. Specific objectives of this research were to identify the photoreactive constituents in water samples taken from various wetland waters and to elucidate the role that these constituents play in the photolysis of the NPS pollutants. The photoinduced degradation of alachlor was tested in several types of agricultural wetland waters. The results from these studies allowed me to identify what were the possible reactive constituents promoting the degradation of alachlor. In series of separate control experiments, I evaluated the factors that control the extent that these constituents will have in promoting the degradation of alachlor. More specifically, I was able to evaluate the role of nitrate, natural organic matter, and iron in promoting the
photodegradation of alachlor. Thus, my results may provide an idea of the role that
photolysis would have in inducing the degradation of recalcitrant compounds in
agriculturally-dominated wetland waters.

3.2 Methods

3.2.1 Materials

All chemicals and reagents were purchased commercially and used without further
purification. Chemicals and reagents were acquired from the following: Alachlor
(99.5%) from Chem Services West Chester, PA; potassium phosphate monobasic from
(KH₂PO₄; Certified ACS reagent), sulfuric acid (Reagent Grade), sodium bisulfite (ACS
Reagent), methanol (Optima), acetonitrile (Optima), hexane (Optima), sodium hydroxide
solution (50 % w/w), and glacial acetic acid (Certified ACS plus) from Fisher Scientific;
potassium phosphate, dibasic powder (K₂HPO₄), sodium phosphate, dibasic
Na₂HPO₄·12H₂O (12-hydrate), sodium phosphate, monobasic monohydrate
NaH₂PO₄·H₂O, from J.T. Baker, INC. (Phillipsburg, N.J.); hydrogen peroxide (30%),
sodium hydroxide (NaOH; analytical reagent) from Mallinckrodt; potassium hydrogen
phthalate (KHP), ferric chloride, sodium borate, p-nitroanisole, and pyridine from Aldrich
(Milwaukee, WI); Leucomalachite green, horseradish peroxidase from Sigma-Aldrich (St.
Louis, MO); Argon (4.8 grade) from Praxair. Suwannee River Fulvic Acid and Lake

99
Frøyell Fulvic Acid from Dr. George Aiken (USGS). Purified water (18 Ω) was produced from a Milli-Q water system (Millipore Corp., Bedford, MA). All glassware and plastic were acid washed either with NOCHROMIX Cleaning Reagent (Godax Laboratories, Inc) in concentrated sulfuric acid or 10% HCL prior to use.

3.2.2 Water Samples and NOM Isolates

The wetland water samples and NOM isolates used for these studies are from the field sites described below. Sampling sites were chosen because of their perceived contamination and reactivity (i.e., NPS contamination from agricultural runoff and potential photoreactive constituents). Two NOM “standards” were also studied to provide a basis for the direct comparison of the results to those of others.

3.2.2.1 Collection and Characterization of Wetland Raw Waters

Wetland water samples were gathered from several field sites that collected drainage water (runoff) from agricultural watersheds. In some cases, samples were collected from natural wetlands, which represented very mature (from a biological and ecological perspective) systems. In other cases, water was collected from constructed wetlands engineered to capture and hold drainage water from agricultural fields to recycle it through sub-irrigation systems (Brown, OSU Extension Experiment). These wetlands differed in their macrophytic communities and, therefore, the variation would be expected
to influence the properties for the NOM derived from these systems. Sampling water from these wetland sites provided a unique opportunity to study the potential for photochemical processes to affect the fate of contaminants pesticides in these waters. Since these systems ranged in their maturity, I hoped that a comparison could be derived that would lead to information regarding how quickly wetlands could develop effective photochemical degradation properties. Experiments were performed in the "raw" water samples and in some cases, solutions consisting of NOM isolated from these field sites.

Old Woman Creek Estuarine Reserve, Huron, OH. Old Woman Creek (OWC) is a natural, 30-hectare wetland located on the south shore of Lake Erie (Figure 3.2) and receives runoff from a predominantly agricultural watershed of approximately 69 km² in size. This wetland receives a significant amount of suspended solids and pesticides (D. Baker, personal communication). A fully-equipped field laboratory at the site was available to provide logistical support for this study. Abundant background on OWC is available from the many previous studies done on the ecosystem (Mitsch, 1989). The site is an "inland freshwater marsh" (Mitsch and Gosselink, 1993) with water depths that range from 0.1 to 3.6 m, and an average depth of 0.5 M, depending on water levels in Lake Erie. NOM concentrations in these waters are high (up to 2 mM organic carbon) due to a high primary productivity (avg. ~ 30 kcal/m²/d) (Mitsch, 1989). The NOM from this site originates from terrigenous (allochthonous) and algal and microbial (autochthonous) sources. Sampling sites were chosen at the inlet (IN), interior (railroad site (RR)), and outlet (OUT) of the wetland; samples were collected at various times during the summer season. Samples could not be collected in the true interior of the wetland in order to
minimize disturbance to the nesting site of bald Eagles per the request of staff at OWC. All samples were filtered (Gelman glass fiber filter (GFF), type A/E) and stored at 4°C until use.

**Fulton County-Shininger Farm Wetland/Reservoir Subirrigation System**

*Project Water; Swanton, OH, Fred Shininger Subsurface Irrigation Project.* The experimental agricultural wetland was created in 1995 as one of three wetlands created to test the effect that recycling drainage water would have on agricultural productivity (L. Brown, personal communication). This wetland captures drainage from 20 acres of subirrigated cropland (Richards *et al.*, 1998). The soil of the area is a silty-clay. The wetland itself is relatively “young” and is sparse in higher order vegetation. From my observations, however, it appeared to be a highly productive system as evidenced by the presence of algal and bacterial mats. Grab samples were collected on August 3, 1999 in 4L amber glass jugs. All samples were filtered (GFF type A/E) and stored at 4°C until use.

**Champaign County, OH, Yocum Farm Subsurface Irrigation Project.** This wetland was constructed in 1997 as part of the OSU Extension program to investigate the utility of using subirrigation to boost crop productivity (L. Brown, personal communication). Subirrigated water flows into the wetland from seeps and subsurface flow as a result of a tile-drainage system. The maximum depth of the wetland was 8 feet. The wetland discharged at a point below this wetland; thus, there was no re-circulation of the water from this system. Little vegetation (macrophytes or algal) was visibly observed in the wetland, although it was in the surrounding areas. Grab samples were collected from the shore of the wetland.
Defiance County-Defiance Agricultural Research Association

Wetland/Reservoir Subirrigation System Project, Defiance, OH. Also constructed in 1995 as part of the OSU Extension program, this wetland collects water from a 27 acre watershed, including runoff from the Defiance County Airport (Richards et al., 1998). The site contains 7 acres of subirrigated cropland. The soil composition is clay. The wetland appeared to be more mature than the other constructed sites. After passing through the wetland, water is pumped to a retention reservoir. Water from the reservoir is then pumped back to the subirrigation zone. Because of better access, grab samples of the water were collected from the reservoir.

VanWert County-Marsh Foundation Wetland/Reservoir Subirrigation System Project. VanWert, OH. This wetland was the third constructed in 1995 as part of the OSU Extension program. It drains the largest area of watershed, 50 acres, which contains 30 acres of subirrigated cropland (Richards et al., 1998). Like the Defiance site, water is stored in a retention basin prior to it being pumped to the subirrigation zones. The soil of the watershed is a silty-clay. Since the wetland was constructed as an upground basin, thus there is no natural flow into the wetland from the surrounding agricultural areas. This wetland was relatively immature as evidenced by the lack of vegetative diversity. Grab samples were collected from the wetland basin.

Suwannee River (SR), Fargo, GA. Grab samples of Suwannee River water were collected at the mouth of the Okefenokee swamp in the Fall of 1999. Water samples were stored on ice and transported to OSU. There, samples were filtered (Gelman GFF type A/E) and stored at 4°C until use.
3.2.2.2 *Characterization of Wetland Water samples*

All samples were analyzed for UV-VIS absorbance, TOC, pH, inorganic anions, alkalinity, and Fe content. UV-VIS absorbance spectra for samples were measured with dual-beam Cary 1 UV-VIS spectrophotometer (Varian). Samples were scanned from 200 to 600 nm in quartz cuvettes having a 1-cm pathlength. The collected absorbance scans were used to calculate attenuation coefficients and light screening factors appropriate for each natural water sample (Figures B.1-8).

Samples were analyzed for total organic carbon (TOC) using a Shimadzu TOC 5000 Analyzer. The TOC analyzer was calibrated using a potassium hydrogen phthalate (KHP) standard in the range of 1-25 mgC/L.

Samples were also analyzed for nitrate, nitrite, chloride, and sulfate via ion chromatography (IC) (Dionex DX-500 IC; Sunnyvale, CA) (APHA, 1995; ASTM 1995). Twenty microliters of natural water sample were injected onto an IonPac AS-11 column (Dionex). A gradient method was used for ionic separation which entailed ramping the mobile phase (85:15(%v/v) H$_2$O : NaOH (0.021 M)) to 15:85 (%v/v), respectively, over a 20 minute period. Concentrations of ions were determined from external calibration curves ($\text{SO}_4^{2-}$ ($0.00004 - 1 \text{ mM, n}=5, R^2 > 0.99$); $\text{Cl}^-$ ($0.0001 - 2 \text{ mM, n}=5, R^2 > 0.99$); $\text{NO}_3^-$ ($0.0001 - 2 \text{ mM, n}=5, R^2 > 0.99$); $\text{NO}_2^-$ ($0.00003 - 0.7 \text{ mM, n}=5, R^2 > 0.99$)). The limit of detection for nitrate in the water samples under our analytical conditions was at $1.0 \times 10^{-7} \text{ M}$. 

104
The pH was measured using an KCl saturated electrode. The alkalinity of the water samples were measured by Gran Titration with standardized 0.05 N HCl (White, 2000; Klarer, personal communication).

Iron (Fe) was measured using a PE4100 ZL transverse heated graphite furnace atomic absorbance spectrophotometer (Perkin Elmer, Norwalk, CT) which utilized Zeeman splitting to separate analyte response from background signal. Atomization of samples was performed at 2100°C and the detection wavelength was set to 248.3 nm. Nitrate (0.015 mg/L) was used as a matrix modifier. Response was calibrated daily to Fe standards that ranged from 0-75 ppb Fe (n=4, R^2 > 0.99). Samples that were found to have concentrations exceeding 75 ppb Fe were diluted to conform to calibration range of the instrument.

3.2.2.3 NOM Isolates

Suwannee River Fulvic Acid (SRFA) This USGS fulvic acid "standard" was isolated from the Suwannee River. Organic matter in the Suwannee River is derived from sphagnum moss and cypress trees (Scott et al., 1998; USGS, 1989). Due to the low pH of the water (~4) there is very little primary productivity in the water column, and as a result, the organic material has little to no contribution from these sources. Thus, SRFA represents an end member NOM. The ^13C NMR data is available (McKnight et al., 1991 and 1994; Ravichandran et al., 1998) and is presented in Table 3.6.
Lake Fryxell Fulvic Acid (LFFA) Lake Fryxell is a perennially ice-covered, oligotrophic lake located in the McMurdo Dry Valleys, Antarctica. Because Lake Fryxell is located in a desert devoid of vascular plants (Scott et al., 1998), the only input of carbon to this system is through microbial or hetero and photoautotrophic sources. Thus, LFFA represents an NOM on the other end of the spectrum from SRFA. The $^{13}$C NMR data for these isolates is published (McKnight et al., 1991) (Table 3.6).

**OWC XAD 8.** Fractionation of NOM from the OWC site was achieved via the XAD chromatography technique described by Aiken and co-authors (1985). This isolate will be used to ascertain the differences in the reactivity of the whole NOM versus the isolated fulvic acid fraction.

**Fulton Co. UF Isolate.** Isolation of this wetland's NOM was achieved using tangential-flow ultrafiltration. Water samples were concentrated with an Amicon CH$_2$ Spiral Wound Ultrafiltration unit equipped with a 1,000 Dalton cut-off membrane. After concentration, metals were removed from isolates by passing the retentate through a proton-saturated cation exchange resin (Bio-Rad AG 50-W-X8). Finally isolates were lyophilized and stored at 4°C until use (Mash, 2001; Everett et al., 1999). Isolates were analyzed by solid-state cross polarization magic angle spinning (CP-MAS) $^{13}$C nuclear magnetic resonance (NMR) analysis (Mash, 2001).
3.2.3 Photolytic Reactions.

The photochemical reactor used is described in Chapter 2 (see Section 2.1.1.1 etc.) with the following differences. The average temperature of the reactor over the course of these experiments increased to 42 ± 3 °C in the photoreactor.

Reaction mixtures were prepared according to the following procedure. A predetermined mass of alachlor (necessary to yield a desired concentration of 5 μM for a given volume) was deposited onto the walls of a glass storage bottle from a stock solution (0.01 M in acetonitrile). All traces of acetonitrile were evaporated under a gentle stream of argon since indirect photolytic processes can generate intermediates that may react with acetonitrile. Alachlor was then dissolved with the appropriate amount of natural water sample, buffered MilliQ water (Millipore Corp., Bedford, MA), or buffered MilliQ water containing NOM isolates. The bottle was gently agitated until alachlor residue was no longer detected on the wall of the storage bottle. The initial concentration (prior to irradiation) of alachlor was measured for each water sample tested to ensure that target concentration (~ 5 μM) was achieved. The reaction solution was then transferred into Pyrex® culture tubes (13 x 100 mm) and placed in the photoreactor for irradiation. Although alachlor has a relatively low Henry's law coefficient (10⁻¹¹ atm-L/mol), test tubes were completely filled with reaction solution to minimize partitioning of alachlor into the headspace of the test tubes due to the high temperature of the reactor. Dark controls were run concurrently; samples were placed in a temperature controlled water bath (42° C). Reactions were carried out at the pH of the natural water sample and in
samples whose pH's were adjusted to between 2 and 8. Test tubes were sacrificed periodically, and reactions were quenched accordingly. All samples from time courses were assayed by either HPLC (Waters), GC/ECD (Fisons 8000 Series), and GC/MS (HP 6890 coupled to HP5873 Mass Ion Selective Detector) for the parent compound and any detectable derivatives.

For HPLC analysis, a direct aqueous injection (100 uL) from sample vials was made onto a 3.0 x 150 mm NovaPak column (60Å, 4 µm reversed-phase (C-18) packing) via Waters 717 plus autosampler. Alachlor was detected via absorbance detection (Waters 486 variable wavelength tunable absorbance detector) at a wavelength of 225 nm (sensitivity at 0.002 M). The mobile phase for the analysis was 60:40 (v/v %) MeCN:H₂O was pumped using a Waters 510 solvent delivery module. Instrument response was calibrated daily using external standards ranging from 0.2 - 8 µM alachlor (n=5, R² > 0.99).

For GC/ECD and GC/MS analysis, 1 mL of the sacrificed sample was extracted with 1 mL hexane in GC/ECD autosampler vials (2.1 mL). Sample and hexane amounts were weighed and actual volumes were calculated based upon densities of aqueous solution (0.9987 g/mL -look up) and hexane (0.659 g/mL) at 20 °C. After addition of hexane, samples were vortex mixed for 1 minute. Experiments designed to test extraction efficiencies under various conditions (high pH, low pH, presence of salts, neutral solution) showed little difference in extraction efficiencies (all methods had slightly > 100% extraction efficiency) with the % RSD for triplicate samples < 3 %. Samples were stored in the freezer until completion of an experiment (storage lasted no more 24 hours).
when the entire sample set could be analyzed by GC. For GC/ECD (CE 8360 GC with ECD (\(^{65}\)Ni as the \(\beta\)-emitter)) the carrier gas was helium (linear velocity at 1.25 cm/s) using nitrogen as the make-up gas at 30 cm\(^3\)/mL. On-column injections of 1 \(\mu\)L were made by the Carlo Erba AS800 autosampler onto a 15 m \(\times\) 0.32 ID \(\times\) 25 \(\mu\)m df RTX-5 (Restek) capillary column. Temperature program for alachlor analysis was as follows: 1 minute at 69 °C, ramp at 15 °C per minute until 280 °C. Retention time for alachlor was 11 minutes.

For the GC/MS the carrier gas was helium set at a flow rate of 1.0 ml/s. One-\(\mu\)L of sample was injected manually into a split/splitless injector that was set to splitless mode. MS detector was calibrated to PFTBA.

3.2.4 Actinometry and Light Intensity Corrections

Light intensity was monitored with chemical actinometry (\(p\)-nitroanisole/pyridine system) (Dulin and Mill, 1982) (See Chapter 2). Because of the light intensity from the photoreactor lamp varied more than 15% over the course of the experiments, it was necessary to develop a correction term that would be used to normalize measured light intensity so that results from different experiments could be compared to one another. A correction term was developed to accommodate for variation in lamp light intensity and was:

\[
\text{Correction Factor} = \frac{(k_{PNA}/\Phi_{PNA})_{\text{avg}}}{k_{PNA}/\Phi_{PNA}}
\]  

(3.3)
The observed rate coefficient for PNA degradation, $k_{PNA}$, was normalized to the quantum yield determined for each experiment, where $\Phi_{PNA} = 0.437[PYR] + 2.82 \times 10^{-4}$ (Dulin and Mill, 1982). The average value, $(k_{PNA}/\Phi_{PNA})_{avg}$, determined from the data from all actinometry experiments was 5.57 einsteins hr$^{-1}$ moles$^{-1}$PNA (n = 42; %RSD = 14.8). Dividing $k_{PNA}$ by the quantum yield normalizes $k_{PNA}$ to the slight differences observed in PNA degradation due to differences in PYR concentration. This average value was divided by the results from the actinometry experiment for a given day to yield a factor that corrects for the variation in lamp intensity. The observed rate coefficients measured for alachlor degradation were multiplied by the factor determined for a given experiment (the actinometer experiment was run concurrently) and allowed for the direct comparison of $k_{obs}$ for alachlor degradation for different experiments. The average light intensity generated from the lamp was found to be 87.1 % of the light intensity of summer sunlight in Columbus OH (at 40°N) assuming a similar distribution of light from the solar simulator as in sunlight. Thus, the irradiation conditions used here approximated both the distribution and intensity of sunlight.

3.2.5 $H_2O_2$ Measurement

Hydrogen peroxide was measured in selected natural waters and NOM isolate solutions using leuco malachite green (LMG) method (Zepp et al., 1988). In this method, a peroxidase catalyzes the oxidation of the dye, leuco malachite green, by hydrogen peroxide according to the following reaction (Figure 3.3) to produce a dye that strongly
absorbs light ($\epsilon_{617\text{nm}} = 80,100 \text{ M}^{-1}\text{cm}^{-1}$). A stock solution of the LMG reagent was made as follows: in a 5 mL volumetric, 2.5 mL of a 2.2 M acetate buffer (pH 4.2), 1 mL of a 4 mg/10 mL-MilliQ horseradish peroxidase solution, and 200 µL of a 33 mg/10mL-MeCN LMG solution were added, and the resulting solution was diluted to the mark with MilliQ water. To measure H$_2$O$_2$ in the µM range, 167 µL of the LMG reagent was added to 2.5 mL of sample. The solution was allowed to react for several minutes, then the absorbance was read in a 1-cm quartz cuvette at a detection wavelength of 614 nm, which proved to be the maximum of the absorption curve on this UV-VIS.

A calibration curve was generated from solutions of Milli-Q solutions of H$_2$O$_2$ that ranged in concentration from 0.1–7.5 µM ($n=6$; $R^2=1.00$). A problem with this method was that the y-intercept significantly differed from 0 (0.12 ABS units). Furthermore, the literature reports that the presence of humic substances suppresses the formation of the green color produced from the reaction of the reagent (Zepp et al., 1988); thus, the results presented from these measurements must be interpreted with caution.

3.2.6 Data Analysis

Data were analyzed using Scientist for Windows v. 2.01 (MicroMath Scientific Software, Salt Lake City, UT) and Sigma Plot 2000 (Jandel Scientific). Rate expressions describing the observed kinetics were solved numerically using the EPISODE package, and observed rate constants for alachlor degradation were determined from least squares

111
fit (Powell algorithm) of the observed kinetic data to the pseudo-first order kinetic model. I did not consider it necessary to correct for alachlor binding to dissolved organic matter since alachlor has a relatively high solubility (242 mg/L @ 25°C; MacKay et al., 1995), and calculations based on the reported soil organic carbon partitioning coefficients, $K_{OC} = 170$ L/kg (Gish et al., 1995; Hornsby et al., 1996), showed that no more than 0.2% of the alachlor present in reaction solutions would be associated with the organic matter present in any of the natural waters or NOM isolate solutions tested, assuming that partitioning will not differ significantly between soil and aquatic NOM (an upper limit estimate).

Iron speciation calculations were performed using PHREEQCI 2.2 version R_0.39 (USGS). Equilibrium constants used were from the PHREEQCI database. The $pK_{a,avg}$ for NOM was assumed to be 5.0. Clearly, this approach provided only a crude estimate of iron speciation; therefore, a more rigorous modeling approach is necessary.

### 3.3 Results and Discussion

#### 3.3.1 Analysis of Natural Water samples

Water samples were analyzed for a number of water quality parameters (Table I). Except for the Suwannee River water, the natural waters tested all had relatively high pH (near pH 8) and corresponded to the moderate alkalinity (reported in mg/L CaCO$_3$)
measured for the same sample set (Klarer, personal communication; White 2000). This data was used to estimate the concentrations of the carbonate species, CO$_3^{2-}$ and HCO$_3^-$, in each natural water tested assuming the alkalinity was due primarily to carbonate species. While it was expected that nitrate would be high in the re-cycled wetland waters, only one sample, OWC 6-2-98 IN, had a significant amount of nitrate present.

The waters ranged a great deal in their TOC content (Table 3.1). Suwannee River water, a "blackwater" stream, had the highest measured TOC at 35.87 mgC/L. The OWC 9-8-98 OUT sample had the lowest TOC (2.17 mgC/L). Of the engineered wetlands, VanWert had the least amount of TOC and this observation is not surprising given the absence of macrophytes and any noticeable algal blooms in the wetland. Fulton Co. and Champaign Co. had the highest TOCs and corresponded to their observed developed microbial and phytic communities.

The UV/VIS absorption spectra obtained for each water are presented in the Appendix (Figure B.I-1). In general, the absorbance increased exponentially as the wavelength decreased from 500 nm to 290 nm and is typical for UV-VIS absorption spectra observed for natural waters (Miller, 1994). Further analysis of these data are discussed in Chapter 4.

The UV/VIS were used to calculate screening factors for polychromatic light and certain molar absorptivities for these waters (Table 3.1). Surprisingly, the Champaign Co. wetland had the highest normalized (to the amount of organic carbon present) molar absorptivity ($\varepsilon_{280\text{nm}}$) at 445 M$^{-1}$ cm$^{-1}$ at $\lambda = 280$ nm. The Suwannee River raw water sample had the second highest measured $\varepsilon_{280\text{nm}}$ (391 M$^{-1}$cm$^{-1}$) as was expected for this
“blackwater” swamp water. The OWC Inlet water had the third highest \( \varepsilon_{280nm} \) (346 M\( ^{-1} \) cm\(^{-1} \)). These \( \varepsilon_{280nm} \)’s were well in excess of those measured for the other natural waters and indicated that the chromophores present in these waters more strongly absorbed UV light relative to the other natural waters tested. In addition to having the lowest TOC, the OWC 9-8-98 OUT water had a relatively low molar absorptivity as reported in Chapter 2.

The waters were found to contain a wide range of iron. The Suwannee River raw water had a highest level of Fe, followed by the OWC 6-29-98 IN water. Two of the waters sampled from the engineered wetlands also had higher Fe levels (Defiance Co. and Fulton Co.). The other samples had significantly less (~10 ppb or less Fe).

Higher alkalinitities observed for the OWC waters were expected. The geology of the OWC site may provide a partial explanation. Wetland sediments were found to be depleted in calcite (CaCO\(_3\)) and dolomite (CaMg(CO\(_3\))\(_2\)) with respect to the suspected source material located in the watershed. The diminution of these minerals suggests that dissolution of source sediments occurred prior to the entry of these grains into the estuary (Frizado et al., 1986) and was presumed to contribute carbonate species in the wetland recharge. Water at equilibrium with calcium and magnesium carbonates would promote a high pH. Biological activity and equilibrium with the atmosphere would also be expected to contribute a significant amount of carbonate species to the water column.

Furthermore, OWC sediments contained more trace elements than in overlying water (Frizado et al., 1986). I expected that these sediments would act as a source of trace metals to the overlying water (either occurring before or after sedimentation). Iron levels in the June OWC sample were quite high as compared to the September samples
sampled from the same year. If trace metals content were due primarily to a contribution from the sediments, then I would have expected the levels of metals to be about the same in the different samples, assuming residence times in the wetland basin were not significantly different. The difference observed in the iron levels measured, however, suggests that it originates from another source, prior to entering the wetland. Total metal concentrations were found to correspond to the turbidity (Klarer, personal communication) and suggests that metals enter the water column through the dissolution of suspended particulates or may exist in colloidal forms. Subsequent analysis of the OWC 6-29-98 IN, OWC 9-8-98 OUT, and OWC 9-14-99 RR showed that they contained 7.45, <1, and 98.60 µg/L Mn, respectively (Doug Beak, personal communication).

The geology of the engineered wetland sites may explain the dissolved species measured. The Fulton Co. sediments were classified as a Nappanee Loam. The soil sample profiles from the site revealed the presence of both iron and manganese oxide in the 19-23 inches deep layer and in the 23-50 inch layer. Also present in the 23-50 inch layer was the presence of calcium carbonate coatings (Larry Brown, personal communication). Of the wetland waters studied, it had the second highest measured alkalinity and third highest level of Fe measured. Measured levels of manganese, however, were quite low, < 1 µg/L. The geological data for the other constructed wetland sites were not obtained.

All of these constituents identified could influence photochemical reactions. While carbonate species are expected primarily to quench photoreactive processes through scavenging (Larson and Zepp, 1988), many trace metals (e.g., Cu, Fe, and Mn)
are photoreactive and could influence pollutant degradation through indirect processes. In addition, waters containing high levels of nitrate (OWC 6-29-98 IN) may also promote photochemical degradation (Mabury and Crosby, 1994).

3.3.2 Photolysis of Alachlor in Agricultural Wetland Waters

In the first set of experiments with alachlor, I wanted to ascertain the likelihood that alachlor would be degraded through light promoted reactions in an agricultural wetland water. Therefore, alachlor was irradiated in different samples of OWC water that varied in concentrations of potentially photoreactive constituents (i.e., nitrate, NOM, and Fe). The OWC waters tested were comprised of a high nitrate, moderate TOC (OWC 6-29-98 IN), a high TOC, low nitrate (OWC 9-14-99 RR) and a low nitrate, low TOC (OWC 9-8-98 OUT) containing samples (Table 3.1). The extent of alachlor degradation was measured using pseudo-first order kinetics. In all cases the $R^2$ for fits were greater than 0.99 indicating the model fit the data reasonably well (Figures B.9-17 in the Appendix). The establishment of a photostationary state of a reactive species could easily account for the first-order kinetics observed while the actual kinetics would be second-order. Until the constituents responsible for the degradation can be identified, and their effect quantified, we cannot ascertain the true kinetics of the system. Still, it is useful to use the pseudo-first order kinetics as a measurable index to gauge alachlor degradation.

Studies were first conducted at the ambient pH (~8) of the natural water samples. Since the work with carbaryl indicated that a pH-dependent indirect photolytic reaction
may occur in OWC water (Ch. 2), the degradation reaction was also tested in water samples whose pH's were adjusted to 4.1 with sulfuric acid. The differences in reactivity between the low and high pH samples were significant (Table 3.1; Figure 3.4). Dark reactions (run in parallel to the light reactions) showed insignificant degradation compared to the reactions performed in the light.

**Direct Photolysis.** Some researchers have suggested that the direct photolysis of alachlor is a pH dependent process (Penuela and Barcelo, 1996) similar to that observed for metolachlor for which the photolysis rate constant was reported to increase with an increase in the pH (Kochany and Maguire, 1994). Direct photolysis control experiments were performed at a low pH and high pH to see whether the direct photolysis component would have a pH dependency in this photochemical system.

Alachlor was irradiated in MilliQ water samples buffered (5 mM total phosphate) at a high (8.08) and low pH (4.21). A slight photoinduced degradation of alachlor was measured at pH 8.08 while no degradation of alachlor was detected above the scatter of the experimental data at pH 4.21 (Table 3.1; Figure B.9a,b). When the experiment at pH 8 was conducted in a 50 mM borate buffer no observable degradation was observed (Figure B.9a). While the results seem to suggest that there may be a pH dependency to the direct photolysis of alachlor, they were not significant enough to draw any firm conclusions. The results did show that Alachlor was not susceptible to significant degradation from direct photolysis on the timescale that these reactions were performed (25 hours). Dark controls run in parallel with the light experiments also showed insignificant degradation. That no significant degradation occurred in these experiments is most likely due to two
factors: 1.) the light intensity of this lamp was much less than used in other experiments and 2.) the timescale of the experiments was not long enough to observe significant measurable degradation above the experimental error. Other researchers who reported the significant direct photolysis of alachlor (measured half-life less than 140 minutes) performed their experiments for up to 15 hours using a light source with a much higher intensity (550W/m²) than that used here (Penuela and Barcelo, 1996; Chiron et al., 1995). When the same researchers irradiated solutions of alachlor in distilled water with sunlight, no degradation of alachlor was detected after five days of exposure. Based upon these results, the direct photolysis component to alachlor's degradation was considered unimportant, and therefore, corrections were not made to measured pseudo first-order rate coefficients.

**Indirect Photolysis.** Since alachlor did not react significantly in the dark or light control experiments, the observed photoinduced degradation of alachlor in the natural water samples can be attributed to indirect photolytic pathways. The results obtained from the carbaryl experiments suggested that a lower pH promoted the degradation of carbaryl in the OWC waters tested; however, the results from the carbaryl experiments did not entirely support a clear pH dependency because of carbaryl's facile dark reaction and its susceptibility to direct photolysis at a high pH. Thus, unlike carbaryl, alachlor should be an excellent probe to study indirect processes because of its insusceptibility to direct and dark pathways.

At the natural pH of the water samples (the unadjusted pH was ~ 8), the sample containing high levels of nitrate reacted most noticeably (6-29-98 OWC IN) in the light
There was a slight promotion measured in the 9-14-99 Railroad water, but alachlor degradation was a little over 8 times less than that observed for the 6-29-98 Inlet water. No significant degradation was observed for the OWC 9-8-98 OUT sample.

Alachlor reacted appreciably more when the pH of these waters was adjusted to a lower value (Figure 3.4; Table 3.1). The observed pseudo-first order degradation rate coefficients increased significantly from those measured at the higher pH's by almost 3 and 10 times for the 6-29-98 IN and 9-14-99 RR water samples, respectively.

The high reactivity observed in the 6-29-98 IN sample may be explained by nitrate photolysis which generates the reactive hydroxyl radical (HO•) (See discussion 2.3.4.1). The reported rate constant for reaction of alachlor with HO• is \(7.0 \times 10^9\) M\(^{-1}\)s\(^{-1}\) (Haag and Yao, 1992). At the high level of nitrate measured in this water (1.01 mM), nitrate photolysis would be expected to play an important role in generating the hydroxyl radical. A pseudo-first order rate coefficient for the degradation of alachlor attributable to a reaction with HO• can be estimated at both pHs assuming the following:

1. The photolysis of nitrate will be the dominant process in generating the HO• in this natural water;
2. Nitrate photolysis is a pH independent process for the range of pHs used in this study;
3. Reaction with HO• is the dominant process degrading alachlor in this water.

These assumptions are reasonable because the level of nitrate measured in the 6-29-98 IN sample is high compared to the other water samples used in this study (Table 3.1) and to natural waters in general (Zepp et al., 1987; Mabury and Crosby, 1994; Wilson and
Mabury, 2000). My work with carbaryl showed that a reaction with HO* generated from nitrate photolysis could account for significant part of the carbaryl degradation in the same water sample (see Chapter 2.3.4.1). Moreover, the literature does not support that nitrate photolysis will have a pH dependency for conditions in which the light source is comprised of wavelengths greater than 280nm (Mack and Bolton, 1999). There is evidence that nitrite photolysis is pH dependent (Fischer and Warneck, 1996; Mack and Bolton, 1999), but the level of nitrite in these samples is so small (< than 0.1 μM), it is not expected to play significant role. The third assumption can't be validated until the results are analyzed.

In general, the rate of change of [HO*] will equal the rate of HO* production ($R_{\text{prod}}$) minus the overall rate of HO* reaction ($R_{\text{rxn}}$) according to:

$$\frac{d[\text{HO*}]}{dt} = R_{\text{prod}} - R_{\text{rxn}}$$

(3.4)

The term, $R_{\text{rxn}}$, is comprised of all the second order processes that lead to scavenging of HO* and can be re-written as:

$$R_{\text{rxn}} = \Sigma k_{\text{HO*,n}} [\text{Scavenger}]_n [\text{HO*}]$$

(3.5)

Assuming constant irradiance and that nitrate photolysis is the only source for HO* production, $R_{\text{prod}}$ and $R_{\text{rxn}}$ will achieve a photostationary state, i.e., $d[\text{HO*}]/dt = 0$, and the concentration of HO* will reach some steady-state value ($[\text{HO*}]_s$).

Under these conditions, then, $[\text{HO*}]_s$ can be determined from the following equation:
[OH•]ss = \frac{R_{\text{PROD}}}{\Sigma k_{\text{HO•, }a}[\text{Scavenger}]_a} \tag{3.6}

The $R_{\text{PROD}}$ of the HO• measured from nitrate photolysis for this photoreactor was $3.01 \times 10^{-7}$ M-HO•/s per molar nitrate (corrected value for lamp intensity) for buffered MilliQ samples (White, 2000). The dominant scavengers of the HO• in the 6-29-98 IN water are expected to be the NOM and carbonate species ($\text{HCO}_3^-$ and $\text{CO}_3^{2-}$). Values for rate coefficients for these species were determined from the literature. An "average" HO• scavenging rate coefficient for DOC was reported to be $2.3 \times 10^4$ L/mgC*s (Brezonik and Fulkerson-Brekken, 1998). Rate constants determined for the reaction of HO• with $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ are $1.2 \times 10^{-7}$ M$^{-1}$s$^{-1}$ and $4.5 \times 10^{-8}$ M$^{-1}$s$^{-1}$, respectively (Schwarzenbach et al., 1993). Concentration of the carbonate species were estimated according to equilibrium calculations based upon the measured pH and alkalinity. In addition, calculations showed that at the concentration used in these experiments (5 µM), alachlor would compete with scavenging by NOM and carbonate species, and therefore, will also contribute to the defining the steady-state level of HO• concentration, i.e.,

$$\Sigma k_{\text{HO•, }a}[\text{Scavenger}]_a = (k_{\text{HO•, DOC}} *[\text{DOC}]) + (k_{\text{HO•, HCO}_3^-} *[\text{HCO}_3^-]) + (k_{\text{HO•, CO}_3^{2-}} *[\text{CO}_3^{2-}]) + (k_{\text{HO•, A}} *[A]) \tag{3.7}$$

From $[\text{HO•}]_{ss}$ the expected pseudo-first order rate coefficient, $k_{\text{pred}}$ can be calculated using:

$$k_{\text{pred}} = 7.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \cdot \frac{60\text{s}}{1\text{min}} \cdot \frac{60\text{min}}{1\text{hr}} \cdot [\text{OH•}]_{ss} \cdot SS \tag{3.8}$$
where $\Sigma S$ is the overall light screening factor determined for $\lambda = 290$ nm to 375 nm (Table 3.1).

Performing this calculation, yields a $k_{pred}$ of 0.0345 $h^{-1}$ and 0.0389 $h^{-1}$ for the pH of 8 and 2.7, respectively. According to these calculations, nitrate photolysis would account for over 100% of the reaction at the higher pH. At the lower pH, however, nitrate photolysis only accounts for about 30% of the observed reaction. If I attempt to do the same calculation for the 9-14-99 OWC water at the high and low pHs, nitrate photolysis accounts for < 7% of the reaction at the high pH and < 1% of the reaction observed at the lower pH. Since this water sample did not contain a high level of nitrate, nitrate photolysis would not be expected to influence strongly the photodegradation of alachlor. For both waters, however, a significant conclusion to draw from these calculations is that the role of nitrate photolysis in bringing about alachlor degradation diminishes at the lower pHs. I did not expect such drastic changes in the dominance of nitrate photolysis in controlling the degradation of alachlor between the high and low pH in the high nitrate sample.

In addition, these calculations indicate that the generation of HO* from nitrate photolysis is not influenced significantly by the alkalinity. The difference in the predicted rate coefficients for the high and low pH samples resulted from the difference in the concentrations of $HCO_3^-$ and $CO_3^{2-}$ at the two pH's. During the reaction solution preparation, solutions were equilibrated with the atmosphere for 24 hours after pH adjustment so as to allow the solution the opportunity to re-equilibrate with the new pH. The pH of adjusted solutions was checked before and after equilibration. The difference
between the predicted pseudo first-order rate coefficients calculated for the higher pH with and without carbonate present was about 7%; thus, carbonate species were not the dominant scavengers of hydroxyl radical in this system. The dominant scavenger of the hydroxyl radical is assumed to be the NOM which accounted for 73% of the scavenging and while alachlor scavenged 20%.

Based upon these calculations, if I compare the reactivity of alachlor in the 6-29-98 IN and the 9-14-99 RR samples, the high nitrate sample went from being greater than 8 times in the high pH sample to less than 3 times more reactive at the low pH than the low nitrate, high NOM sample. For the high pH samples, it would seem reasonable to assume the difference in reactivity was primarily due to the differences in nitrate level driving the reaction, and the presence of a high amount of NOM, which under these considerations is expected to act primarily as a HO• scavenger. Accordingly, if I assume the same level of nitrate is present in the 9-14-99 RR sample as in the 6-29-98 IN sample, the \( k_{\text{pred}} \) would increase to a value that is 63% of that observed for the 6-29-98 sample.

At the lower pHs, the data suggests that another mechanism leading to alachlor degradation is initiated for both samples. This alternate mechanism has the effect of making the \( k_{\text{obs}} \)'s measured for the different waters closer in value than those observed at the higher pH. If this hypothesis is true, then it would appear the promotion is related to the NOM since the reaction in the higher NOM sample was promoted at the lower pH to a greater extent than the lower NOM sample (Table 3.1; Figure 3.3). While these results do not necessarily invalidate my third assumption (i.e., that HO• is the predominant
transient reacting with alachlor), they do demonstrate the need to identify the reactive species causing alachlor degradation at the lower pH.

*Engineered Agricultural Wetlands.* In using alachlor as a probe for indirect photolysis, I wanted to ascertain whether or not the pH effect observed for the degradation of carbaryl and, now, alachlor is a local effect (specific to the OWC water), or a general phenomenon due to the photochemical reactivity of certain water constituents common to most natural fresh waters. In order to test this question, several water samples were collected from various wetlands across Ohio that capture drainage from surrounding agricultural (Fulton, Co., Van Wert, Co., and Champaign, Co.) and municipal (Defiance Co.) areas. For comparison, experiments were also conducted in Suwannee River (SR) raw water (pH 4.26).

Alachlor degradation was measured in all these samples at their natural and adjusted pH according to the same procedure used for the OWC samples. Again, pseudo first-order kinetics fit the observed degradation rather well with $R^2$'s over 0.99 for all light experiments (Table 3.1) (Time courses are presented in the Appendix B.13-17a,b).

As in the OWC samples, alachlor was degraded more efficiently in the light for all samples (Figure 3.5). Dark reactions run in parallel with the light experiments showed no significant degradation of alachlor (not statistically different from zero). Thus, indirect photolysis, as promoted by the constituents present in these wetland waters, like in OWC case, is apparently the major pathway for degradation of alachlor. The order of reactivity at the natural pH for the wetland waters was Champaign Co. > Defiance Co. > Van Wert Co. > Fulton Co. The half-life of alachlor determined for these waters ranged
from as much as 12 to 4.6 days in this photochemical reactor system. These half-lives would translate to 25 to 12 days in sunlight, assuming an 8-hour irradiation period, and indicates that the photochemical degradation process is not all that efficient at ambient pH levels. The reactivity of these systems would be aided by the presence of excess nitrate, as was seen in the OWC 6-29-98 IN sample ($t_{1/2} = 0.86$ days in photoreactor or 2.3 days in sunlight).

At the lower pH, the photolysis of alachlor was again promoted. The order of reactivity observed for this sample set was: SR > Fulton Co. > Defiance Co. > Champaign Co. > VanWert Co. It is interesting to note that the Fulton Co. water went from being the least reactive to the most reactive water of the engineered wetlands. The level of promotion at the lower pH was different for each water tested (Table 3.1) and mirrored the order of reactivity. The SR sample had the highest measured half-life for the photoreactor system, at $t_{1/2}$ of only 6 hours. The half-lives ranged from 9.4 hours to 2.3 days for the highest to lowest reactivity measured in the engineered wetland water. Dropping the pH significantly improves the overall degradation of alachlor in these waters.

It is difficult from this data to attribute the photoreactivity of a particular water sample to a particular water constituent. Though the Defiance Co. water had approximately the same level of iron and nitrate as the very reactive Fulton Co. water, its reactivity toward alachlor was substantially less. The TOC in this water, however, was less than Fulton Co. sample and may be the primary reason for the decreased reactivity. The Defiance Co. water was, however, substantially more reactive than the VanWert Co.
water which had a similar amount of TOC, but much less measured Fe. The alkalinity of these waters was higher than that measured in the OWC waters (Table 3.1) and indicated that this could play a more important role in the scavenging of HO• by CO₃²⁻ and HCO₃⁻ at the higher pH.

Nitrate levels measured in this set of water samples was found to be very low in these waters (Table 3.1). At the level of nitrate measured, indirect photolysis arising from nitrate photolysis would be expected to be minimal (at most, 3% for the high pH Champaign Co. sample). Even so, when the pH is lowered, photochemical degradation is significantly enhanced (Table 3.1). Since direct photolysis of alachlor does not occur to a significant extent at the low pH, these results also provided evidence that another photochemical mechanism other than nitrate photolysis is responsible for producing the reactive intermediates that are leading to alachlor degradation.

3.3.3 Identification of Potential Reactive Transients

Indirect photolytic processes have been found to be primary the cause for the photochemical degradation of alachlor in the wetland waters tested. As was discussed previously (Section 1.2) several reactive transients can be generated from the photolysis of natural water constituents and include: (1.) NOM triplet states reacting with ground state alachlor through energy or electron transfer processes; (2.) excited state NOM reacting with oxygen to form reactive oxygen species (e.g., HO•, 'O₂, H₂O₂, O₂⁺, e⁻) that, in turn, react with alachlor; (3.) the interaction of metals (either associated with organic
ligands present in NOM or free species in the water column) in promoting Fenton or photo-Fenton type chemistry that would promote the production of HO• in this system.

Several experiments were designed to probe the reactive transient(s) responsible for the degradation of alachlor. The OWC 9-14-99 RR water sample was chosen for this study because it degraded alachlor effectively at low pH, even though there was very little nitrate present. In the event that the reaction is promoted through either NOM triplet states or through reactive oxygen species (ROS), a change in the oxygen level in the reaction solution should have a pronounced effect on the reaction. In the former case, oxygen (a triplet in its ground state) reacts efficiently with other triplets to quench them. If the reaction occurs through reactive NOM triplet states, then reducing the concentration of oxygen in solution should cause the observed reaction rate coefficient to increase significantly. Finally, if hydrated electrons were important in promoting the reactions, then reducing the oxygen level would result in a promotion of the reaction since oxygen scavenges the hydrated electrons very efficiently, with a reported rate constant of 1.8-2.2 × 10¹⁰ M⁻¹ s⁻¹ (Fisher et al., 1987; Cooper et al., 1989). Conversely, if ROS such as superoxide or singlet oxygen are important intermediates, then a reduction in O₂ should result in a dramatic inhibition of the observed rate coefficient (Canonica et al., 1995). Thus, in the first of this series of experiments, the effect of oxygen on the observed degradation was tested by reducing the concentration of dissolved oxygen through the sparging of reaction solutions for at least 1 hour prior to the irradiation. Although argon sparging would not completely eliminate oxygen from the solution, it would reduce oxygen’s concentration significantly thereby affecting any process promoted by oxygen’s
presence. To test the efficacy of H$_2$O$_2$ (an important photo-product of NOM) to promote the reaction, alachlor was irradiated in a solution containing 265 units of catalase. Catalase promotes the dismutation of H$_2$O$_2$ into O$_2$ and H$_2$O, and therefore, would quench any effect that H$_2$O$_2$ would have in promoting the reaction (Vaughan and Blough, 1998).

These studies, however, would yield little information regarding the role that the HO$^\cdot$ may play in facilitating these reactions. I felt the most effective means of determining the effect of this intermediate would be to shut the pathway down by adding a scavenger that would outcompete alachlor for the HO$^\cdot$. Methanol has been used in several studies as a specific HO$^\cdot$ probe (White, 2000; Zhou and Mopper, 1990; Mopper and Zhou, 1990). It has been reported to be relatively unreactive with other ROS (Zhou and Mopper, 1990) and with hydrated electrons (Anbar and Hart, 1964) and therefore, would be a good choice to use in this study. To test the importance of HO$^\cdot$ in facilitating the degradation reaction, a reaction solution was spiked with 0.0599 M methanol (MeOH). Given that the rate constant for reaction of MeOH with HO$^\cdot$ is 9.8 x10$^8$ M$^{-1}$s$^{-1}$ (Zhou and Mopper, 1990), the amount of MeOH added to each experiment should outcompete other scavengers for HO$^\cdot$. It should be noted that at the concentration of MeOH used in this study, the alteration of the NOM chromophoric properties due to polarity changes would be minimal. This was confirmed by the fact that an overlay of the molar absorptivities of the reaction solution with and without MeOH showed no significant shifts (Figure 3.6).

The role of metals in promoting these processes was also investigated. It was assumed that if the level of metals present in the water were reduced, then a
corresponding reduction in alachlor reactivity would be observed if metals were important in mediating the transformation process. The removal of metals from the raw water was accomplished by passing a split of the raw water sample (1 L) through a proton-saturated cation-exchange resin (Bio-Rad AG 50-W-X8) in order to reduce the level of cations present in the solution. The pH of the proton saturation solution was adjusted to 4.14. This sample is referred to as the OWC 9-14-99 RR H+ saturated water in the rest of this text.

The H+ saturated solution contained at most 5.55 ppb Fe (Table 3.5) and indicated that the cation exchange resin was about 56% efficient in removing the Fe from the water sample. Thus, a large percentage of the Fe measured in the OWC water (about 44%) existed in a non-labile form (possibly strongly-bound to the NOM). Similar results were observed when the 6-29-98 OWC Inlet water was passed through a cation exchange column. In that case, the proton-saturated water sample had 54.48 ppb Fe compared to the original sample which had 134.01 ppb Fe yielding a removal efficiency around 59%. In addition, the process also removed approximately 18% of the TOC. The loss of this TOC changed the chromophoric properties of the water slightly, as evidenced by the difference in the measured molar absorptivity for this water (Figure 3.6).

For all experiments, alachlor degradation fit pseudo-first order kinetics reasonably well \( (R^2 = 0.99) \). Data from these experiments are compared to those attained from the original experiments with this water (Table 3.2 and Figure 3.7). Dark controls for all experiments showed no significant degradation of alachlor.
The results from these experiments can provide insight as to the reaction mechanism. Argon sparging of the pH adjusted raw water inhibited the reaction by approximately 39%. In addition, alachlor was also irradiated in a solution of Fulton Co. NOM isolate that was argon-sparged prior to the reaction. In this case, alachlor degradation was again inhibited by almost 41% (Table 3.2), about the same level of inhibition observed for the OWC 9-14-99 RR water. When MeOH was added to the raw water, the reaction was completely quenched (no detectable degradation of alachlor was measured). The addition of catalase to the raw water did not inhibit the reaction; the rate coefficients determined were not statistically different from the pH adjusted raw water. Finally, irradiation of alachlor in the H+ saturated water inhibited the reaction by approximately 25% when determined pseudo-first order rate coefficients were normalized to the TOC.

The quenching of the reaction induced by argon sparging excludes bimolecular reaction with NOM triplets and the hydrated electron as the dominant reactive species. The results suggest that oxygen plays a minor role in facilitating these reactions. Because the inhibition was observed for two types of water samples (a raw water and an NOM isolate), the reactive pathway appears to behave consistently. There are several pathways by which O2 could facilitate the reaction. The photolysis of NOM could result in the reduction of dissolved O2 to form O2•− and ultimately, H2O2, or could produce ¹O2 or alkylperoxyl radicals (ROO•) through either reaction of excited state NOM with O2 or the addition of oxygen to carbon-centered radicals. Hydrogen peroxide is fairly unstable in natural waters and can act as an oxidant, or, can be photolyzed to form HO•. All of these
species are fairly reactive. It is assumed, however, that if any of the species were the dominant reactant, then more of inhibition of the reaction would have been observed. For example, Faust and Hoigné (1987) report that phenol oxidation by ROO\(^{•}\) was inhibited by a factor over 100 when reaction solutions were argon sparged prior to irradiation.

The addition of MeOH completely inhibited the reaction indicating that HO\(^{•}\) was the primary reactive species responsible for transforming alachlor. If HO\(^{•}\) was produced from the ejection of this species from excited state NOM, a dependency on the oxygen concentration would not be expected. Since almost 60% of the reaction was not quenched by argon sparging, such a mechanism may be important and results in the transformation of alachlor in this water. Because of the specificity of methanol for the HO\(^{•}\), ROS and other NOM-radical species can be discounted as important intermediates. Canonica and Freiburghaus (2001) reported that the addition of propanol (which would react identically to methanol as an HO\(^{•}\) scavenger) did not quench photochemical processes that were speculated to result from reactions of substituted phenols with NOM triplets and NOM radicals (carbon- or oxygen-centered) and lends support to my conclusion that HO\(^{•}\) is the primary reactive radical in this system. To the best of my knowledge of the literature, there is no known report of the reaction of alachlor with either superoxide or singlet oxygen. The results with the MeOH also provide further evidence that the hydrated electrons are not involved in alachlor degradation since MeOH reacts very slowly with hydrated electrons (k < 1 x 10\(^4\) L mol\(^{-1}\) s\(^{-1}\)) (Anbar and Hart, 1964) and would not be expected to quench the reaction. Indeed, aqueous solutions containing up to 20% MeOH had no measurable effect in reducing steady-state levels of
hydrated electrons (Anbar and Hart, 1964). These results, however, do not preclude the importance of other species that may influence the hydroxyl radical concentration in the light. It is not known, for example, how alkylperoxyl radicals (ROO*) can react with MeOH, though I found no evidence in the literature of such a reaction.

The role of H$_2$O$_2$ remains difficult to ascertain from these experiments. Argon sparging of the reaction solution would be expected to inhibit the production of H$_2$O$_2$ and could potentially shut-off any reaction pathways promoted by H$_2$O$_2$. Hydrogen peroxide may also react with reduced metal species to form HO* through the Fenton pathway and any reduction in H$_2$O$_2$ production would minimize this process. Either interpretation would be supported by the argon sparging results. The results from the experiment with the catalase, however, suggest that H$_2$O$_2$ is not an important intermediate. I do, however, question the validity of these results since I did not test either the thermal or photolytic stability of catalase under the environmental conditions of the photoreactor. A control experiment was performed in which alachlor degradation was measured in a buffered MilliQ water containing 5 μM H$_2$O$_2$. The rate coefficient observed under these circumstances was quite high (0.0363 hr$^{-1}$) which could account for a large percentage (81%) of the observed rate coefficient in the pH adjusted raw water. Since alachlor did not react appreciably in the dark with this same level of H$_2$O$_2$, light is necessary to drive the reaction. These results do support the idea that H$_2$O$_2$ could be an important species in generating hydroxyl radical in this photoreactor system. It is difficult to ascertain how important H$_2$O$_2$ photolysis would be in natural waters, since the presence of other water constituents tend to outcompete H$_2$O$_2$ for photons since the molar absorptivity of H$_2$O$_2$ is 132
< 1 M⁻¹cm⁻¹ above wavelengths > 300 nm (Haag and Hoigne, 1985). Thus, any contribution from its direct photolysis to HO* production would be expected to be minimal in natural waters.

The results from the experiment with the H+ saturated water showed that metals did have an important contribution to the overall reaction. I assumed initially, that the biggest effect of metals would be in promoting Fenton and photo-Fenton chemistry to generate the reactive hydroxyl radical. At the lower pH of these experiments, oxidation of Fe(II) by oxygen would be expected to be slow, and therefore, would be available to react with H₂O₂ through Fenton chemistry to form HO* (Voelker et al., 1998). There is also the possibility that certain metals could bind with alachlor to form photoreactive ligand-to-metal charge transfer bands, but if this were the dominant process controlling the reaction, it would not be expected to be influenced by the presence of MeOH. Since the reaction is completely quenched by the addition of MeOH, the dominant role of metals must be to promote HO* formation. Because the removal efficiency for the cation exchange process was fairly low a good estimate of that contribution by metals cannot be ascertained, and I wonder what the inhibition would have been had I been able to completely strip the raw water of metals. Even so, this experiment shows that metals are important in mediating the reaction, and, taken in consideration with the other control experiments, their primary role seems to be generating the hydroxyl radical.

The assumption that the hydroxyl radical is the reactive transient is supported by work that has been previously conducted in this laboratory. White (2000), was able to measure the production of HO* from several of these waters and their isolates at both a
low and high pH using two different molecular HO• probes, MeOH and DMSO. For the water samples that were tested at the higher and lower pHs (OWC 9-14-99 RR and OWC 6-29-98 IN) the data showed the production of HO• increased significantly in both waters by 1.93 and 2.45 ×’s, respectively. Calculating a hypothetical steady-state concentration of hydroxyl radical from the measured pseudo-first order rate coefficient for the OWC 9-14-99 RR from my results at a pH of 4.08 yields a value (1.77 × 10⁻¹⁵ M) that closely corresponds to the value predicted (2.11 × 10⁻¹⁵ M) from the measured HO• production rate for this water at the same pH using this photoreactor system (White, 2000).

These data support the idea that HO• generated either directly from the photolysis of the NOM or by some other mechanism is the dominant transient responsible for the reaction of alachlor, and that the pH dependency is related to a more efficient production of HO• at a lower pH. On the basis of these results, it seems reasonable to conclude that reactive transient responsible for alachlor’s transformation is HO•.

3.3.4 Discussion

The data for all the water samples indicated the photodegradation of alachlor is significantly improved by lowering the pH of the natural water samples. The relationship between the pH and photochemical behavior may be due to some common reactivity associated with a “bulk” constituent, such as natural organic matter, which, although not identical among different water samples, could share in similar functional groups resulting in similar chemical behavior. In addition, the pH behavior could be due the
presence of other common constituents, such as metals (like iron), that could promote the formation of reactive intermediates. At this point, the specific photosensitizers causing the promotion have not been identified but it is noted that these wetland waters all behave similarly in their promotion of the photochemical degradation of alachlor at lower pHs.

Inspection of the water quality data reveals three primary constituents that are common to all the waters tested and may behave as dominant precursors to reactive species: nitrate, NOM, and iron. In the water sample where alachlor reacted the fastest, nitrate was present at high levels (~ 1 mM). Alachlor reacted the second fastest in the Suwannee River raw water, which had the highest measured TOC and the highest measured iron levels. Furthermore, the 9-14-99 water, which had a high TOC but relatively low Fe levels (compared with other samples having similar low pH reactivity), also reacted relatively efficiently at a lower pH. The Fulton Co. water, which had slightly more iron than the OWC 9-14-99 RR water but about the same level of TOC reacted slightly faster than the OWC 9-14-99 water at the lower pH. Finally, a H+ saturated sample of the OWC 9-14-99 RR water had a lower reactivity (normalized to the amount of organic carbon present) than the raw water at the same pH. Thus, all three of these species are suspected to play some role in the degradation of alachlor.

The influence that these constituents have in promoting alachlor degradation was mediated by the pH. Even with samples containing a high (~ 1 mM) concentration of nitrate, showed that nitrate photolysis, while controlling the reactivity of the water at a high pH, is NOT the dominant HO• precursor at low pH. These findings were supported by the results from the low nitrate containing wetland water samples, where up to 99%
alachlor transformation could be attributed to processes other than nitrate promoted reactions. Thus, the results from the reactions run in the agricultural wetland waters suggested that the NOM may act as an important HO* producer in a photochemical reaction that is promoted at low pH.

The factor that alachlor degradation is promoted by lowering the pH can be evaluated for a given water sample by calculating the ratio of $k_{obs}$ at pH 4 to that at pH 8. When promotion factors were calculated for all the tested water samples, they differed significantly (Table 3.1). This result suggests that one or more constituents were contributing to and/or inhibiting the observed reactivity and controlling the extent of the observed reaction. The 9-14-99 OWC RR and the Fulton Co. water samples had the largest promotion factors at 9.6 and 5.5, respectively. Examining the data in Table 3.1 shows that, in general, the promotion corresponded to the level of the TOC, i.e., the greater the [TOC], the greater the observed promotion when the pH was lowered (Figure 3.8). The correlation for the linear regression fit of this data was 0.823. The Champaign Co. water sample did not fit this trend and is presented as an outlier to the linear regression fit. The large screening factor and high alkalinity of the Champaign Co. sample may explain, in part, why it does not follow the trend. These data suggest that NOM is necessary for a second, significant light-promoted reaction at the lower pH.

When the data from the different pHs were treated separately a correlation (when outliers were removed) was observed at the high pH between the TOC and alachlor transformation while at the lower pH, a much lower correlation is observed (Figure 3.9 a,b). Even removing the same samples that were outliers in the pH 8 sample set did not
improve the fit ($R^2$ value drops to 0.31). This finding suggests that processes resulting from the direct photolysis of the NOM alone cannot entirely account for the increase reactivity at the lower pH, and that perhaps the NOM behaves synergistically with some other constituent that is not accounted for by this analysis. The data also suggests that the reactivity at the higher pH (in the absence of clearly photoreactive species such a nitrate) may be due entirely to processes arising directly from the photolysis of the NOM. The data from the OWC 6-29-98 samples were not included in these plots because of the contribution that nitrate had on the measured rate coefficient.

Being that measured TOC is a bulk measurement, I cannot identify its specific photoreactive component. Vaughan and Blough (1998) reported that the highest quantum efficiency for hydroxyl radical production from the NOM they tested occurred at a wavelength near 320 nm. If absorption of light by NOM at this wavelength were important for generating reactive transients for our waters, then a correlation between the molar absorptivity (normalized to the amount of organic carbon present) at 320 nm determined for the waters tested in this study versus $k_{obs}$ should exist. When $k_{obs}$'s were plotted against the molar absorptivities measured at 320 nm and 280 nm (which is a wavelength often used as an index of aromatic character of the NOM), trends were observed that were opposite those obtained by plotting $k_{obs}$'s vs TOC. At the higher pH, $k_{obs}$ was poorly correlated ($R^2 < 0.40$) to the molar absorptivity at both 320 nm and 280 nm whereas at the lower pHs, a much better correlation ($R^2_{280nm} = 0.91; R^2_{320nm} = 0.93$) was obtained (Figure 3.10 a, b). The slope of the 320 nm plot ($5.50 \times 10^{-4}$ M·cm/hr) was higher than that determined at 280 nm ($3.24 \times 10^{-4}$ M·cm/hr) and suggests that the
reaction is more sensitive to changes in molar absorptivity at 320 nm than from changes at 280 nm. This would make sense if the chromophore responsible for the reactivity had its maximum near this wavelength and a tailing absorbance into the far UV regions.

In order to test the importance of a pathway driven solely by the natural organic matter, alachlor was irradiated in reconstituted XAD-8 OWC NOM isolates (cation-exchanged material) (Aiken et al., 1985). Two solutions were prepared by diluting a stock solution of OWC XAD-8 isolate to concentrations of 9.20 and 9.46 mgC/L in a phosphate buffer (pH 4) and a borate buffer (pH 7), respectively (Table 3.1). These solutions were irradiated and alachlor degradation was measured. As with the natural waters, the rate of alachlor degradation was enhanced at the lower pH (Figure 3.11; Table 3.1). The pseudo-first order rate coefficient, k_{obs}, measured at the lower pH was 2.1 times larger than that measured at the higher pH (Table 3.1).

Given the differences in the TOC and other water constituents for the natural waters (Table 3.1), it is noteworthy that the measured k_{obs} for the NOM isolate solutions at both pHs fall within the range observed for the natural water samples, and, at the lower pH, was very similar to those measured for water samples of similar composition (low nitrate, low iron, higher TOC water samples (i.e., OWC 9-14-99 RR, Champaign Co.) (Figure 3.10). The larger rate coefficient observed at the higher pH for the XAD-8 solution compared to those measured for the other the natural waters (except for the high nitrate sample (OWC 6-29-98 Inlet)), could be due to the lack of carbonate species in artificial solution. The results from the XAD studies seems to suggest that the NOM itself could be the primary source for the reactive intermediate (assumed to be HO•; see Section
3.3.3) causing the alachlor degradation in the light. White (2000) reported that the hydroxyl radical production rate of this same isolate at a pH of 4 was $4.00 \times 10^{-11} \text{ M HO}^*/\text{s per mgC/L}$. Multiplying this value by the TOC (9.20 mgC/L) provides a prediction of the HO* production rate expected for this experiment. Applying equations 3.4 and 3.6 to this production rate results, $k_{\text{pred}}$ of $0.0286 \text{ hr}^{-1}$ or almost 98% of that actually observed for this water (Table 3.1). Thus, the prediction based upon hydroxyl radical production from this water alone accounts for the overall reactivity observed for this NOM isolate and provides further support that the reactive intermediate transforming alachlor is the hydroxyl radical.

The significant reaction of alachlor in the reconstituted OWC XAD-8 isolate solution suggests that metals play a minor role in promoting the degradation of alachlor. The protocol for isolating NOM using XAD-8 resin calls for the stripping of labile metals from the isolated materials by passing the XAD-8 extract through a proton-saturated (or sodium-saturated) cation exchange resin (See Chapter 2.3.4.2 discussion on this topic). The resulting eluent is fairly “clean” of most of the metals associated with the original organic material. However, there is always a small fraction of the metals that are irreversibly bound to the organic matter and are referred to as the non-labile fraction. Thus, there will never be a truly “clean” organic matter isolate, and therefore, no conclusions can be made regarding the influence of metals on the reaction until it is established that there is a minimum concentration of metals needed to induce an observable effect. This concentration limit was the subject of further investigation (See Section 3.3.8).
Therefore, it cannot be ruled out that the promotion of rates observed at lower pH may also be due, in part, to the presence of metal species, either free or associated with the organic matter. I measured total iron (Fe\textsubscript{T}) in these water samples as an indicator of the amount of metals present in these samples. In comparing these samples, the OWC 9-14-99 RR sample, which had the largest factor of promotion, contained Fe\textsubscript{T} at a level (~12 ug/L) four and half times lower than the Fulton Co. sample which had 55 ug/L Fe\textsubscript{T}. This observation seems to suggest that the promotion at the lower pHs is not related to the amount of total iron present. Indeed, if the factor promotion versus the measured Fe\textsubscript{T} for the samples in plotted, no correlation exists (Figure 3.12) unlike that obtained for the TOC (Figure 3.8). There is also little correlation if Fe\textsubscript{T} is plotted versus k\textsubscript{obs} at either the high (R\textsuperscript{2} = 0.09) or low pH (R\textsuperscript{2} = 0.39). These results suggest that total iron does not influence the reaction, but does not rule out the possibility that complexed iron is important.

The observed rate coefficient for the degradation of alachlor in the pH adjusted natural waters did correspond well with the ratio of total Fe (ppb) to TOC (mgC/L) (Figure 3.13). Included in this sample set are the results from the reaction run in the H\textsuperscript{+} saturated OWC 9-14-99 RR water and in a split of the proton-saturated water that was spiked with Fe\textsuperscript{3+} (at 2 μM) (Figure 3.13). The OWC 9-14-99 RR raw water was slightly more reactive than the proton saturated sample for the given the ratio of Fe:TOC, and the Fe-spiked water, with even a higher Fe: TOC ratio, was substantially more reactive than both other samples, thus, providing further evidence that Fe does have a role in promoting the reaction possibly as a complex. Contrary to the results from the XAD experiments,
these plots suggest that NOM primarily acts as a quencher. However, given the likelihood that the Fe present is associated with the NOM and the previous results showing a positive correlation between TOC level or measured molar absorptivities and observed rate coefficients, the presence of organic matter must also be important in promoting the reaction. These data suggest that Fe and NOM are somehow linked in the observed reactivity and suggest the involvement of both Fe and NOM in the observed degradation of alachlor.

Based upon these results, the obvious question to resolve is to identify the mechanism(s) through which NOM mediates this reaction. Does it behave primarily as an HO• scavenger, or, through its association with Fe, a promoter of the indirect transformation of alachlor?

In summary, alachlor was found to be degraded through indirect photochemical pathways in several natural and artificial wetland waters and in DOM isolate solutions. Control experiments tentatively identified the reactive intermediate primarily responsible for degradation of alachlor to be the hydroxyl radical. The data indicate that NOM promotes this degradation process and that the extent of the NOM promotion is dependent upon the pH. The results suggest that iron also has a role in promoting alachlor degradation in a reaction that is dependent on the [TOC]. The promotion of alachlor degradation at low pH suggests that lowering the pH activates photochemical degradation mechanisms that are unproductive at high pH.
3.3.5 Role of NOM in Mediating this Reaction

In order to evaluate the role that the OWC NOM was playing in these reactions, I studied the photoinduced degradation of alachlor in solutions comprised of reconstituted OWC XAD-8 isolate. The material was chosen for study because I wanted to isolate the effect of the NOM on the reaction from that of other constituents (e.g., iron) that may promote alternative pathways for alachlor degradation. In addition, preliminary experiments with this isolate demonstrated that it promoted the degradation of alachlor in the light (see Section 3.3.4).

In this series of experiments, I studied the effect that varying the NOM concentration would have on the measured pseudo-first order rate coefficient, $k_{\text{obs}}$, for alachlor degradation. The description of the water quality parameters for these samples are presented in Table 3.3. When $k_{\text{obs}}$ is plotted against the [TOC], the value $k_{\text{obs}}$ increases linearly and then begins to plateau (Figure 3.14). Such behavior is typically observed in reactions involving reactive transients and is consistent with the interpretation that NOM plays a dual role in these types of systems, i.e., that NOM acts as a source and sink for reactive transients (Faust and Hoigné, 1987). Increasing the NOM initially causes a direct response in the observe rate coefficient (linear regions); but the addition of more NOM to the system results in a higher scavenging efficiency and the NOM begins to outcompete the probe (in this case, alachlor) for the HO• thereby depressing the observed rate coefficient for the probe.
In order to ascertain whether this was a valid interpretation for the current study, the data were modeled according to the dual-role theory of NOM behavior. The timecourse plots demonstrated that alachlor degradation fit pseudo first-order kinetics very well \((R^2 > 0.99)\). Thus, the rate of alachlor degradation \((\frac{dA}{dt})\) can be expressed as:

\[
\frac{dA}{dt} = -k_{obs}[A]
\]  

(3.9)

Assuming that \(HO^*\) was the principal reactive transient, \(k_{obs}\) can be expressed as:

\[
k_{obs} = k_{al}[HO^*]
\]  

(3.10)

where \(k_{al}\) is the rate constant for the reaction of alachlor with the hydroxyl radical which is reported to be \(7.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}\) (Haag and Yao, 1992). Since I used the purified XAD-8 isolate of the OWC water, I assumed that the NOM is the only precursor to the photochemical formation of \(HO^*\). The concentration of \(HO^*\) will reach a photostationary state under conditions of constant irradiation of invariable intensity, and the assumption that the production rate will not vary during the course of the experiments. Thus,

\[
\frac{dHO^*}{dt} = k_{prod}[DOC] - k_{DOC}[DOC][HO^*] - k_{al}[A][HO^*] - \Sigma k_s[S][HO^*] = 0
\]  

(3.11)

where \(k_{prod}\) is the NOM-dependent production rate coefficient for the formation of \(HO^*\) from this XAD-8 isolate. The value for \(k_{prod}\) has been previously determined for this material in this photochemical reactor system and was \(3.99 \times 10^{11}\) moles \(HO^*\) per second per mgC/L (White, 2000). Processes leading to the loss of \(HO^*\) from the water would include scavenging by the NOM and unidentified "bulk" scavengers \((S)\) where \(k_{doc}\) and \(k_s\) represent the scavenging rate coefficients by DOC and S, respectively. Reaction
with alachlor would also lead to the loss of HO*, and at the level of alachlor used in this study, would be a process that would compete with scavenging by the NOM and bulk scavengers. Once the level of HO* reaches its photostationary-state value ([HO*]ss and equation 3.11 can be rearranged to yield:

\[
[\text{HO*}]^{\text{ss}} = \frac{k_{\text{prod}}[\text{DOC}]}{k_{\text{DOC}}[\text{DOC}] + k_{\text{als}}[A] + \Sigma k_s[S]} 
\]  

(3.12)

Substituting this expression into equation 3.10 yields:

\[
k_{\text{obs}}(\text{hr}^{-1}) = \left( \frac{k_{\text{als}}k_{\text{prod}}[\text{DOC}]}{k_{\text{DOC}}[\text{DOC}] + k_{\text{als}}[A] + \Sigma k_s[S]} \right) \times \frac{3600 \text{ sec}}{\text{hour}} 
\]  

(3.13)

The known variables, [DOC] (I used the TOC for this value), [A], and k_{als} were substituted into this equation, and the model was “fit” to k_{obs} using least squares analysis (Scientist, Micromath). The value for the scavenging rate constant for the DOC with HO* was allowed to be determined from the best fit of the data since the literature reports a range of reactivity for DOC with HO* in which scavenging rate coefficients have been reported to vary from \(1.0 \times 10^4 - 1.0 \times 10^5 \text{ (mgC/L)}^{-1} \text{ s}^{-1}\) (Hoigné and Bader, 1978; Hoigné and Bader, 1979; Haag and Hoigné, 1985; Hoigné et al., 1989; Zepp et al., 1992; Haag and Yao, 1993; Brezonik and Fulkerson-Brekken, 1998; Westerhoff et al., 1999). Without including the consideration for another “bulk” scavenger, the model did not adequately describe the data. Thus, the “bulk” scavenger term was included in the model, and \(\Sigma k_s[S]\) was also determined from the best fit of the data.

The results from this model are shown as the solid line in the plot (Figure 3.14). The model described the observed behavior fairly well (\(R^2 = 0.99\)) when k_{obs} was
corrected for inner filter effects (white circles). Thus, the data is consistent with dual-role model for NOM, *i.e.*, that dissolved NOM is acting both as the initiator and scavenger of the photoreactive transients that react with alachlor to induce the degradation. The fitting exercise returned values for $k_{DOC}$ of $1.20 \times 10^4$ L mgC\(^{-1}\)s\(^{-1}\) and for $\Sigma k_i[S]$ of $1.13 \times 10^5$ s\(^{-1}\).

The value determined for $k_{DOC}$ fell within the range reported for other DOCs and provided support that this model adequately represents the data. No clear trends are evident between $k_{obs}$ and either $F_{ET}$ ($R^2 = 0.35$) or $F_{ET}$ normalized to TOC ($R^2 = 0.07$) levels for this data set, and therefore, the total iron apparently does not influence these reactions significantly. These results suggest that NOM isolate alone is primarily responsible for the observed light-promoted degradation of the alachlor although they do not rule out the involvement of unidentified Fe-NOM complexes. If trace levels of Fe-NOM complexes promoted the reaction, a similar curve (Figure 3.14) would still be expected because of NOM's role as a scavenger.

The inclusion of the term for the "bulk" scavenger ($\Sigma k_i[S]$) accounted for the scavenging of HOC from species other than alachlor or the NOM. While including this "correction" factor implies that there was error in the fit, it is not unreasonable to assume the presence of other scavengers in these solutions other than alachlor or the NOM. For example, contaminants that scavenge HOC may have been introduced to the reaction solution with the addition of alachlor or the buffers. Furthermore, potential scavengers may also include the buffers themselves, anions introduced into solution during the pH adjustment (with $H_2SO_4$), or transients produced during the photoreaction. Dihydrogen phosphate ($H_2PO_4^-$), the dominant buffer species for these reactions (at pH 4.3), has been
reported to have a rate constant for reaction with hydroxyl radical from $2.2 \times 10^4$
(Maruthanmutha and Neta, P., 1978) to $1.2 \times 10^7$ (Farhataziz and Ross, 1973) M$^{-1}$s$^{-1}$. The buffer concentration used in these experiments was 5 mM, which could account for a substantial fraction (up to 53%) of the “bulk” scavenging rate coefficient. Not only would I expect scavenging from the buffer and contaminants present in the alachlor solution plated out on the preparation flask, but also could expect scavengers arising from photochemical processes. Transient scavengers would include H$_2$O$_2$ ($k_{H_2O_2} = 1.2 \times 10^7$
M$^{-1}$s$^{-1}$ (Farhataziz and Ross, 1973)), superoxide ($k_{O_2^-} = 10^4$ M$^{-1}$s$^{-1}$ (Farhataziz and Ross, 1973)), hydroperoxyl radical ($k_{HO_2^-} = 5 (\pm 1.5) \times 10^9$ M$^{-1}$s$^{-1}$ (Farhataziz and Ross, 1973)) which are common transient species produced photochemically in oxygenated solutions during irradiation of natural organic matter. Overall, “bulk” scavenging of the HO$^*$ accounts for 59% of the scavenging at the lowest TOC to 33% of the scavenging at the highest TOC.

Faust and Hoigné (1987) reported a similar trend for the DOM (Contech fulvic acid) sensitized degradation of trimethylphenol (TMP). In this paper, they attribute the reactivity of TMP to reactions with organic peroxyl radicals (ROO$^*$) produced from the irradiation of solution with light $> 290$ nm. However, it should be noted that all their reactions were performed in solutions containing not only the fulvic acid but also 0.2 μM Fe, 1 nM Mn, and 1 nM Cu. These metals are now known to participate in photo-Fenton and Fenton chemistry to produce the hydroxyl radical (Zepp et al., 1992; Voelker and Sedlak, 1995). Even so, their paper showed a very similar trend to that observed here for
the alachlor reactivity: that at low concentrations of DOM (< 5 mgC/L), $k_{\text{sens}}$ (observed rate coefficient for NOM photosensitization) increased linearly with the TOC, then departed from linearity at higher TOC concentrations. This behavior was attributed to the scavenging behavior of the NOM; at low levels, NOM did not compete efficiently for the reactive radicals and therefore, did not control the transient species lifetime (and hence, steady-state levels). At higher concentrations, the NOM competed effectively to reduce the lifetime of the transient species reacting with the TMP. The modeling exercise performed here is consistent with that interpretation as well, even though the suspected reactive transient is of a different nature.

In addition, the effect of oxygen on the reactivity of the OWC XAD-8 isolate was tested. The rate coefficient observed for alachlor degradation (0.0282 hr$^{-1}$) in a solution containing 5.73 mgC/L of the isolate did not differ significantly from what would have been predicted based upon the model calculations for this NOM (Figure 3.14). Thus, argon-sparging had little effect on the reaction of alachlor with the OWC XAD-8 isolate. This result is significantly different from the effect that oxygen had in Faust and Hoigne’s experiments, where the observed degradation of their target compound was significantly diminished (by at least 100x’s) in argon-sparged solutions.

The small difference between the $k_{\text{obs}}$ measured in the argon-sparged solution and the predicted value in air-equilibrated solutions indicates that the reactive transient arises solely from photolysis of the NOM. Hydroxyl radical production from irradiation of NOM has been the subject of several recent studies (White, 2000; Vaughan and Blough, 1998, 1999). One mechanism proposed to explain the production of HO• involved the
photochemical reactivity of quinone moieties present in the NOM matrix. A number of water-soluble, substituted benzoquinones (used as analogues for naturally occurring quinones) generated hydroxyl radical in aqueous solutions in a mechanism attributed to the either electron transfer or hydrogen abstraction from water (Alegria et al. 1999; Alegria and Ferrar, 1997) according to the following equation:

$$^3\text{BQ}^\cdot + \text{H}_2\text{O} \rightarrow \text{BQ}^- + \text{HO}^- + \text{H}^+$$  \hspace{1cm} (3.14)

Vaughan and Blough (1998) proposed that such a mechanism may be occurring from triplet states of quinone moieties incorporated into the NOM (Vaughan and Blough, 1998; 1999). They note that the chromophoric properties of quinones are consistent with such a mechanism since they have an absorption band that falls within the same wavelength region (~ 320 nm) where they observed the maximum efficiency for hydroxyl production (Vaughan and Blough, 1998). They also reported similar aerobic and anaerobic quantum yields which provides further evidence of a process arising strictly from the photolysis of the NOM. However, this observation also presents a fundamental problem to their proposed mechanism. If the reactivity of the NOM arose from triplet states, then I would have expected a substantial increase in the quantum yield under anaerobic conditions because oxygen is a known triplet quencher. If, however, the triplet was quenched predominantly by another constituent (or water) through collisional deactivation (Wayne, 1988) then the quantum yields would be independent of oxygen concentration. Furthermore, if the reactivity was due to a quinone-type NOM moieties, I would not have expected to see the pH dependency in the alachlor reaction with the XAD-8 isolate.
The observation that the degradation coefficient of alachlor is independent of the oxygen concentration for the OWC XAD-8 isolate solution contrasts with the findings for the raw waters in which a decrease in the observed rate coefficient was observed in argon-sparged solutions (Section 3.3.3). Iron, however, was present at relatively higher levels in the raw waters and oxygen mediated reactions may be expected to play a larger role in those systems. Moreover, the rate coefficients measured for the XAD-8 isolate system more closely corresponded to the natural waters containing little to no Fe or nitrate.

Finally, the corrected (for light screening effects) $k_{obs}$ was normalized to the [TOC] in each reaction solution. When plotted against the TOC level, the value of this factor decreased with an increase in TOC. The fairly good correlation ($R^2 = 0.949$) (Figure 3.15) provides further support that the role of TOC as a scavenger becomes more important at the higher levels of TOC. The data suggests that alachlor is being out-competed for transients by the TOC.

The data presented here is consistent with the dual-role model for NOM acting as a precursor and scavenger of photochemically-produced reactive transients. No correlation was observed between the level of $Fe_T$ and $k_{obs}$ and suggests little role for iron, although this does not preclude that Fe-NOM complexes at trace levels may be playing a role. Taken together with the results that the reactivity of alachlor in this NOM isolate was dependent on pH (Table 3.1), the results indicate that pH adjustment activates a mechanism associated with the photolytic properties of the NOM.
3.3.6 Role of Hydrogen Peroxide

One aspect of these experiments that remains unclear is the role that hydrogen peroxide (H$_2$O$_2$) plays in mediating these reactions. Once H$_2$O$_2$ is formed there are a number of ways it can react to produce reactive transients. First, H$_2$O$_2$ is a relatively unstable transient itself. Often it will act as an oxidant of organic substrates to form water and O$_2$. H$_2$O$_2$ also undergoes direct photolysis to form hydroxyl radicals according to:

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{hv}} 2\text{HO} \cdot
\]

This process is generally discounted as being important in natural waters since H$_2$O$_2$ only weakly absorbs light of $\lambda > 290$ nm (Cooper et al., 1989). H$_2$O$_2$ can also oxidize the reduced forms of metals to produce the higher valent metal and the hydroxyl radical in either Fenton or photo-Fenton reactions (Voelker and Sedlak, 1995; Zepp et al., 1992). Iron and copper are two metals that promote Fenton chemistry and have been well studied. Vaughan and Blough (1998) suggested that up to 50% of the production of HO• from SRFA isolate could be due to the photo-Fenton system.

The pathway for the production of H$_2$O$_2$ from DOC has been proposed to be (Scully et al., 1996; Cooper et al., 1994):

\[
\begin{align*}
\text{DOC} \xrightarrow{\text{hv}} & \text{DOC}^* \\
\text{DOC}^* \xrightarrow{\text{inc}} & \text{DOC}^* \\
\text{DOC}^* + \text{O}_2 & \rightarrow \text{DOC}^* + \text{O}_2 \cdot^- \\
\text{HO}_2 \cdot & \leftrightarrow \text{O}_2 \cdot^- + \text{H}^+ \quad (pK_a = 4.8)
\end{align*}
\]
\[ \text{HO}_2^- + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  
(3.20)

\[ \text{HO}_2^- + \text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^- \]  
(3.21)

\[ 2\text{O}_2^- + \text{H}_2\text{O} \leftrightarrow \text{O}_2 + \text{HOO}^- + \text{HO}^- \]  
(3.22)

Ground state DOC, \( ^1\text{DOC} \), absorbs light \((h\nu)\) to form the excited singlet state \((^1\text{DOC}^*)\) (3.13). \(^1\text{DOC}^*\) undergoes intersystem crossing (isc) to form the longer-lived triplet state \((^3\text{DOC}^*)\) (3.14) which, in turn, can react with \( \text{O}_2 \) to form either superoxide anion \((\text{O}_2^-)\) or perhydroxyl radical, \( \text{HO}_2^\cdot \) (3.15-16). Both \( \text{O}_2^- \) and \( \text{HO}_2^\cdot \) dismutate into hydrogen peroxide (3.17-19). Superoxide is known to have a high proton affinity (more than just in the acid-base sense) because of its redox-driven propensity to want to exist as \( \text{O}_2 \) (Sawyer, 1991). Therefore, superoxide acts as a strong Brönsted base. Although these pathways are theoretical, they can provide clues as to the variables that control \( \text{H}_2\text{O}_2 \) chemistry in natural waters (Scully et al., 1996).

In order to assess the importance of \( \text{H}_2\text{O}_2 \), alachlor was irradiated in the presence of 5\( \mu \)M \( \text{H}_2\text{O}_2 \) in buffered \((pH = 4.0)\) MilliQ water. The measured rate coefficient for photodegradation of alachlor in the \( \text{H}_2\text{O}_2 \) control solution was very similar to that measured in some of the solutions (Table 3.4). The reaction is apparently promoted in the light, as a dark control produced no degradation of Alachlor. These results indicated that the photolysis of \( \text{H}_2\text{O}_2 \) to produce \( \text{HO}^- \) could be important in facilitating these reactions.

In order to investigate this effect, hydrogen peroxide was measured in three reaction solutions that differed significantly in their ability to facilitate alachlor degradation.
degradation. If H\textsubscript{2}O\textsubscript{2} photolysis were important, then the measured levels of H\textsubscript{2}O\textsubscript{2} should correspond to observed reactivity in a way that is consistent with this idea. H\textsubscript{2}O\textsubscript{2} was measured in the OWC XAD-8 isolate (9.20 mgC/L) solution at pH 4, the OWC 9-8-98 OUT (2.17 mgC/L) sample at pH 8, and the OWC 9-14-99 RR sample at pH 4 and the unadjusted pH (TOC =11.3 mgC/L). The results are plotted (Figure 3.16). The OWC XAD-8 isolate had the highest levels of H\textsubscript{2}O\textsubscript{2} measured: it was found to be almost 5 μM after only 2 hours of irradiation and reached a maximum of 8.5 μM after 20 hours of irradiation in this lamp (these experiments were conducted for 25 hours). The OWC 9-8-98 Outlet water had a maximum of about 1.1 μM of H\textsubscript{2}O\textsubscript{2}. The maximum amount of H\textsubscript{2}O\textsubscript{2} measured in the OWC 9-14-99 RR water at the ambient pH of the raw water (8) and in pH adjusted water (4) was 4.7 and 0.33 μM, respectively. At these H\textsubscript{2}O\textsubscript{2} levels, the scavenging of the HO\textsuperscript{*} by H\textsubscript{2}O\textsubscript{2} would be expected to be quite low. Indeed, at the highest level measured, scavenging by H\textsubscript{2}O\textsubscript{2} would account for less than 0.1% of the “bulk” scavenging term as discussed above (Section 3.3.5). Therefore, the primary role of H\textsubscript{2}O\textsubscript{2} in this photoreactor system could be to produce the hydroxyl radical through photolysis or other secondary reactions (Fenton chemistry). If H\textsubscript{2}O\textsubscript{2} was rapidly being photolyzed to produce the dominant share of HO\textsuperscript{*} in these systems, I would expect to measure very low (if even detectable) concentrations of H\textsubscript{2}O\textsubscript{2} in all of the systems. The results from the reaction in the OWC 9-14-99 RR water at pH 4 are consistent with this interpretation because the sample contained much less H\textsubscript{2}O\textsubscript{2} than the other two samples and it was the most reactive toward alachlor photodegradation having a k\textsubscript{obs} of 0.0447 ± 0.00535 hr\textsuperscript{-1}. 

152
On the other hand, for the OWC XAD isolate solution (pH 4), \( H_2O_2 \) increases over time until it reaches a relatively, high steady-state concentration (~ 8 \( \mu M \)). Such behavior indicates that, initially, the \( H_2O_2 \)'s reaction rate is slower than its formation rate. I would expect to see an accumulation of \( H_2O_2 \) in the XAD solution if the production rate of \( H_2O_2 \) from the XAD isolate was significantly greater than the production from the 9-14-99 OWC RR (pH 4 or 8), or, if \( H_2O_2 \) reacted to a lesser extent in the XAD solution than in the 9-14-99 OWC RR water. In addition, I would not have expected to see the pH-dependency of the \( H_2O_2 \) accumulation exhibited by the OWC 9-14-99 RR water.

Scully et al. (1996) showed that production rate of \( H_2O_2 \) from several different types of natural waters correlated very well in a power function \( (R^2 = 0.94) \) to the level of DOC (for measured DOC's < 10 mg/L), regardless of the sample source. Outliers of the plot were samples that contained high levels of iron (> 500 ppb Fe). The authors attributed the failure of these samples to conform to the plot to the facile reaction of iron with \( H_2O_2 \) through Fenton chemistry. These findings present some interesting implications for this work. First, if the production rate of \( H_2O_2 \) is dependent only on the level of TOC for samples containing low amounts of iron, then for the samples tested here, I would expect that the production rate of \( H_2O_2 \) to obey the following order: OWC 9-8-98 OUT < OWC XAD-8 < OWC 9-14-99 RR. This would indicate that the \( H_2O_2 \) production rate for the OWC XAD-8 would be smaller than that for the OWC 9-14-99 water, and the cause for the greater accumulation of the \( H_2O_2 \) in the OWC XAD-8 solution could not be due to the difference in production rates. Furthermore, the expected production rates also contradict the observation that \( H_2O_2 \) accumulated to a greater extent
in the OWC 9-8-98 water than in the OWC 9-14-99 (pH 4) water. Again, at the comparative levels of TOC, I would have expected the latter sample to have much more H$_2$O$_2$. Thus, differences in H$_2$O$_2$ production rates do not explain the accumulation trends.

The cause for the observed differences in H$_2$O$_2$ accumulation must be due to the reactivity of the H$_2$O$_2$ in the samples. The molar absorptivity of the NOM is much higher for the XAD-8 than the OWC 9-14-99 RR samples and perhaps more efficiently screens light from the H$_2$O$_2$ to prevent its photolysis. This explanation seems reasonable until I consider the results from OWC 9-8-98 OUT which possessed a significantly lower molar absorptivity (Table 3.1). For this sample, I would have expected to see little to no H$_2$O$_2$ accumulation, yet H$_2$O$_2$ accumulated to a level above 1 μM. In addition, the 1.05 × difference measured in the molar absorptivities (at λ =280 nm) for the OWC 9-14-99 RR high and low pH samples (Table 3.1) does not seem to be significant enough to explain the 14 × difference observed in the H$_2$O$_2$ concentration between these two samples. Thus, an H$_2$O$_2$ photolysis mechanism does not adequately explain the loss of H$_2$O$_2$ from the water.

Information regarding the production of HO* in these samples and from H$_2$O$_2$ may be useful in understanding these results. The production rate of HO* (R$_{\text{prod,HO*}}$) from H$_2$O$_2$-spiked MilliQ, OWC 9-14-99 RR and the OWC XAD-8 were measured in this photoreactor (Table 3.4) (White, 2000). The production rate normalized to the amount of H$_2$O$_2$ was determined to be 2.75×10^{-12} moles HO* per μM H$_2$O$_2$ per second (White, 2000). From this normalized production rate, a maximum expected R$_{\text{prod,HO*}}$ from H$_2$O$_2$
can be calculated for each sample using the highest level $\mathrm{H}_2\mathrm{O}_2$ measured for each sample. Given that the production rates of hydroxyl radical were also measured for these samples (except for the OWC 9-8-98 Outlet) sample, we can compare the predicted production rate due to $\mathrm{H}_2\mathrm{O}_2$ photolysis only to the actual HO* production rate. For the water samples tested, less than 6.5% of the HO* production rate could be accounted for by photolysis of $\mathrm{H}_2\mathrm{O}_2$. Hence, $\mathrm{H}_2\mathrm{O}_2$ photolysis is not expected to an important source of HO* in these samples.

These calculations support the findings from the earlier experiments in which I tested the importance of $\mathrm{H}_2\mathrm{O}_2$ in promoting alachlor degradation by quenching the $\mathrm{H}_2\mathrm{O}_2$ pathway by adding excess catalase to the reaction solution (Section 3.3.4). I observed very little inhibition of the observed rate coefficient; the $k_{\text{obs}}$ for the catalase system was 90% of the observed rate coefficient for the OWC 9-14-99 RR water and indicated that at most, $\mathrm{H}_2\mathrm{O}_2$ pathway could account for 10% of the indirect photolysis.

The data obtained from argon sparging experiments (Section 3.3.4) offers an alternate explanation for the trends observed here. If most of the $\mathrm{H}_2\mathrm{O}_2$ is produced through the photolysis of NOM and subsequent reaction with $\mathrm{O}_2$, then argon sparging should inhibit its formation and impact on the observed reaction. The data showed that argon sparging inhibited the reaction in the natural waters tested by 40% (Table 3.2) but did not have a statistically measurable effect in the NOM isolate solution (Figure 3.14). One of the major differences between the water samples and the NOM isolate solution was the presence of iron. If part of the production of HO* were dependent on Fenton chemistry, then the presence of iron would be important in promoting this process.
The data from the \( \text{H}_2\text{O}_2 \) measurements is consistent with a Fenton chemistry mechanism. First it explains why the level of \( \text{H}_2\text{O}_2 \) accumulated to the greatest extent in the XAD-8 system where \( \text{Fe}^+ \) was below the limit of detection. The results from the OWC 9-14-99 RR experiment can also be explained by this mechanism. This water had 10 times more iron present than that measured in the other samples (Table 3.1) and thus, should have an observable effect. At pH 8, an accumulation of \( \text{H}_2\text{O}_2 \) is observed whereas at pH 4, \( \text{H}_2\text{O}_2 \) never accumulates significantly. The Fenton mechanism is expected to exhibit a pH dependency because the oxidation of iron (II) species by oxygen is a pH dependent process (Stumm and Lee, 1961; King, 1998). At high pH, this oxidation occurs quite rapidly and will outcompete \( \text{H}_2\text{O}_2 \) for reaction with Fe(II). At low pH, however, the kinetics for oxygen oxidation of Fe(II) species slows appreciably and Fe(II) oxidation by \( \text{H}_2\text{O}_2 \) can occur more readily. In the OWC 9-14-99 RR water, at a pH of 4, \( \text{H}_2\text{O}_2 \) never reaches an appreciable level suggesting it is being rapidly consumed whereas at a higher pH, \( \text{H}_2\text{O}_2 \) accumulates significantly in the system. This is the type of pH trend I would expect based upon Fenton chemistry. Finally, The 9-8-98 sample had levels of iron that were undetectable and the experiment was performed at high pH. Thus, the Fenton pathway would be minimal for this sample, and due to the low TOC, the \( \text{H}_2\text{O}_2 \) production would also be small. Hence, a steady, slow accumulation of \( \text{H}_2\text{O}_2 \) would be expected for this system, which was what I observed. Thus, the participation of \( \text{H}_2\text{O}_2 \) in Fenton chemistry may be the most significant way it influences the light-promoted reaction of alachlor in these natural waters as suggested by Vaughan and Blough (1998).
The hypothesis that H$_2$O$_2$ photolysis is unimportant in these reactions fails to explain why the control experiment (alachlor in 5 μM H$_2$O$_2$ solution) is so reactive. Based upon H$_2$O$_2$ normalized production rate of HO$^\cdot$ from H$_2$O$_2$, $k_{prod}$ determined for the control experiment (0.009 hr$^{-1}$) severely underestimated the value measured (0.0363 hr$^{-1}$). This indicates that the photolysis of H$_2$O$_2$ could not explain the observed rate coefficient, and suggested that a contaminant was introduced to the reaction solution that was responsible for the observed reactivity. Introduction of iron into the solution could have occurred from the buffer, or even the H$_2$O$_2$ reagent itself. Analysis of the reaction solution for iron showed the solution contained 1.09 ± 0.31 ppb Fe. If iron is important in catalyzing Fenton Chemistry at very low levels, it could have a significant impact on the reactivity of alachlor in this solution.

These results suggest that the direct photolysis of H$_2$O$_2$ is insignificant in the indirect photolysis of alachlor while its participation in Fenton chemistry may play a larger role. The occurrence of Fenton chemistry also provides an explanation for the observed pH dependency of these reactions. In order to understand how important Fenton chemistry will be in these systems, the influence of the pH and trace metals on these reactions must be evaluated.

3.3.7 The pH Dependency

In order to better assess the cause for the pH dependency, reactions were run in three types of samples in a pH range of 2-8. The samples tested were the OWC 9-14-99...
RR H+ (proton-saturated) water, the SRFA reconstituted isolate, and a NOM isolate of the Fulton Co. water. The Fulton Co. NOM was isolated in our laboratory using ultrafiltration (Mash, 2001). After concentration, it was passed through a cation exchange resin and finally, lyophilized. While this procedure would not result in de-salting the sample (there is no concentration gradient established for small ions during ultrafiltration), it did concentrate the organic matter between the molecular weight cutoffs of 0.7 μm and 1000 Daltons, and provided an NOM sample representative of the whole water (Mash, 2001). The Fulton Co. isolate and the OWC 9-14-99 RR H+ water were chosen because alachlor was fairly reactive in the corresponding raw waters. The SRFA isolate was chosen because of its purity and it has been extensively used in reactivity studies.

The reason these samples were studied instead of the raw water samples was to minimize the influence that metals would have in these reactions since metals are known to have a pH dependent photolytic mechanism (Zepp et al., 1992; Faust and Hoigne, 1990; Faust and Zepp, 1993; Voelker et al., 1997). Thus, I wanted to see if the pH had an effect when reactions were promoted solely by NOM. Unfortunately, isolation of the NOM from metals proved very difficult; when the samples were run on THGFAA, all had detectable levels of iron, and in the case of the Fulton Co. isolate, iron was quite high (Table 3.5).

The results showed that the photodegradation of alachlor was promoted in all the samples at all pHs (Table 3.5). Comparing the $k_{obs}$ determined at a pH 8 with that for pH 4, the Fulton Co. water, which had the lowest measured TOC (~3.5 mgC/L) and greatest level of Fe (~40 ppb), had the largest promotion (4.8×'s) at the lower pH. The OWC 9-14-
99 RR H+ (~ 2ppb Fe; ~9.1 mgC/L) had the next highest level of promotion (3.8 x's), followed by the SRFA (~1ppb Fe; ~10.3 mgC/L), which had the least (1.3x's).

Plots of k_{obs} (hr⁻¹) versus the pH for each sample tested show that there is little difference between the k_{obs} in the pH range from 6-8 for each sample type AND between all samples (Figure 3.17). It is striking that the plots overlay so well in the pH region greater than 6 given the differences in measured TOC and iron between the Fulton Co. sample and the other samples. The RSD for k_{obs} measured for the SRFA, Fulton Co., and OWC 9-14-99 H+ samples between these pHs was 3.2%, 3.7% and 2.0%, respectively. In general, though, at the highest pH measured, the ranking of reactivity increasing order was Fulton Co. < OWC 9-14-99 RR H+ < SRFA, which corresponded to the level of TOC measured in the samples.

Once the pH was adjusted to values lower than 6, however, the plots significantly diverge. Thus, the pH dependency of k_{obs} is not a linear function but rather has a non-linear dependence in which k_{obs} increases exponentially at lower pH’s and reaches an asymptotic low level at the higher pH. The only other pH trend recorded for processes that were mediated by NOM was an exponential decrease was observed for the rate of a reaction promoted by singlet oxygen at higher (> 9) pHs (Zepp et al., 1981).

The exponential increase in k_{obs} with a decrease in pH was observed for all the samples studied. Thus, whatever is promoting the reaction may be common to all the samples (even though the source of the NOM’s may be very different). The common constituent could be either a particular type of reactive chromophore in the NOM whose
photochemical reactivity is pH dependent (something that has not been reported), or metals.

The Fulton Co. water showed the most sensitivity to a change in the pH. This sample also had a correspondingly higher level of iron. The SRFA and OWC 9-14-99 samples showed similar behavior and had a similar level of iron present in the samples. Since the TOC levels were quite different for the samples, \( k_{\text{obs}} \) were normalized to the TOC (Figure 3.18). Again, the Fulton Co. system showed the most sensitivity and changed to a greater extent than what was observed for the other two samples. The effect of normalizing the \( k_{\text{obs}} \) to the TOC on the plots for the SRFA and the OWC 9-14-99 RR H\(^+\) resulted in excellent agreement between these two samples. Because the levels of iron were different among the samples, \( k_{\text{obs}} \) observed was also normalized to the \( \text{Fe}_T \) (Figure 3.19) to yield a pseudo-3\(^{rd}\) order rate coefficient. The plots for the SRFA and the OWC 9-14-99 RR H\(^+\) water became very scattered and suggested that normalizing the \( k_{\text{obs}} \) to \( \text{Fe}_T \) essentially resulted in producing a coefficient that was independent of the pH. This interpretation must be taken with caution since the propagated error was substantial for these samples (because the iron measurements were so low). If this interpretation is valid, however, these results imply that iron, even at the relatively low levels found in these samples (~1 ppb) was important in promoting these processes at a low pH. The Fulton Co. sample, however, gave noticeably different results: the normalized \( k_{\text{obs}} \) still was found to be dependent on the pH.

In regard to the pH dependency of the photochemical reactivity of the NOM itself, perhaps some information regarding source materials can be beneficial in understanding
the reactivity of the samples. For the OWC 9-14-99 RR H+ and Fulton Co. samples, the systems from which both samples were derived are characterized by what appears to be a high primary productivity. In the Fulton Co. site, algal mats were visible upon sampling. Similarly, measured primary productivity in OWC was found to be quite high (avg. ~ 30 kcal/m²/d) (Mitsch, 1989). In general, the NOM from systems with higher primary productivity will have more aliphatic and less aromatic moieties in the NOM substrate relative to that which is terrestrially derived. The aromatic characteristics are borne out in the molar absorptivity data, i.e., the molar absorptivity at λ = 280 nm has been shown to correspond to the level of aromaticity in natural water samples (Chin et al., 1994). Therefore, the lower the molar absorptivity, the less aromatic (and presumably, more aliphatic) a NOM is. Both the Fulton Co. sample and the OWC 9-14-99 RR H+ have molar absorptivities that are similar in magnitude and indicates similarity in source NOM. Synchronous Scan Fluorescence Spectroscopy (SSFS) supported the contention that the isolate from Fulton Co. was primarily of microbial and algal origin (Mash, 2001).

The SRFA, in contrast, has a much higher molar absorptivity and indicates that this NOM contains a higher % of aromatic content derived from terrestrial sources. The pH is so low in the Suwannee River that the environment is not favorable to pelagic primary production. Data from ¹³C NMR measurements of these samples (Table 3.6) provides further evidence that supports these ideas. The samples arranged in increasing order of aromaticity based upon the ¹³C NMR data are: Fulton Co.< OWC XAD-8 (used as an analog for the NOM expected in the OWC 9-14-99 RR H+ sample) < SRFA. Similar rankings are obtained when the samples are placed in increasing order of %
carboxylic acid and % carbonyl. The opposite ranking (i.e., SRFA < OWC < Fulton Co.) is obtained from the % aliphaticity data. Thus, the $^{13}$C NMR data showed that the OWC NOM is less like the Fulton Co. NOM as previously though based upon the molar absorptivity data and in fact, would appear to be of intermediate character between the mostly microbially derived Fulton Co. sample and the terrestrially derived SRFA. In general, then, the ranking of the reactivity at the highest pH (from Figure 3.17 and 19) corresponds to the trends of aromaticity, carboxylic acid, and carbonyl content in the NOMs which suggests that NOM would be primarily responsible for the reaction at the higher pHs rather than promotion by iron.

Indeed, at the high pH, there was little difference in the alachlor photodegradation between all the samples. Given that there was almost a 10-time difference in the level of total iron between the Fulton Co. sample and the other samples, the data suggests that the reaction at a high pH is insensitive to the iron. Thus, these results provide further support that iron is not important in promoting the degradation of alachlor at a high pH.

At the lower pHs, however, a number of factors could be influencing the reaction of alachlor. Primarily, the pH will affect both the speciation of metals (iron), including both labile and bound (by organic ligands) forms, and metal reactivity (Zepp et al., 1992; Faust and Zepp, 1993; Faust and Hoigné, 1990). Furthermore, the pH will also affect the NOM conformation (Schlautman and Morgan, 1993). A change in pH could lead to a change in photochemical properties (Bruccoleri et al., 1993) and/or binding capacity of an NOM for alachlor, as speculated by Chiron et al. (1995).
The differences observed in the photodegradation of alachlor at the lower pHs between the samples clearly corresponded with measured iron and TOC levels. The SRFA and OWC 9-14-99 RR H+ samples were most reactive when compared with the Fulton Co. isolate solution having a pseudo-3rd order rate coefficients at pH 4 that were 4-7 x's higher than the Fulton Co. isolate (Figure 3.18). The difference between the SRFA and OWC 9-14-99 RR H+ water cannot be evaluated given the error associated with the calculation (i.e., they are statistically indistinct). While the SRFA and OWC samples were the most reactive in promoting alachlor degradation, the Fulton Co. sample proved to be the most sensitive to changes in the pH: i.e., the factor of promotion determined from the pseudo-3rd order rate coefficients calculated from the pH 8 and 4 data was largest for the Fulton Co. isolate (6.9) followed by the OWC sample (6.1) and finally, the SRFA (5.1).

The sensitivity of the sample to the pH may have more to do with the than the iron than the NOM. The Fulton Co. water had approximately 10x's more Fe than the other two samples and also had the largest measured kobs (hr^-1), regardless of the fact that it had the lowest level TOC of the samples. Any process promoted by Fe and dependent upon the pH would be expected to have a compounded effect (~ 10x's) in this sample.

It is also interesting to note that the total iron measurements showed some general trends as a function of pH. In each case, iron levels had a "U"-shaped profile across pH's studied, a profile that would be expected based upon the Fe speciation for the given pH range (Figure 3.17). The total Fe will be higher at lower pHs in aqueous solutions because both Fe^{2+} and Fe^{3+} are stable. In the mid- to high pH ranges, Fe^{2+} is efficiently
oxidized to Fe$^{3+}$ by O$_2$, and Fe$^{3+}$ reacts with OH$^-$ to form insoluble Fe hydroxides or polymers. These can precipitate-out leading to a reduction in the total Fe measured in the water column (based upon the analytical technique used for these samples). It has also been suggested that at the mid-pH ranges, NOM ligands will more efficiently bind with iron than HO$^-$ thus keeping it in solution in the form of soluble complexes. At the lower pHs, NOM will become protonated and have less sites available iron complexation. If DOM complexes are forming to a great extent for these samples, then the reduction in measured Fe could be due to sorption of the Fe-DOM complexes on the glass walls of reaction test tubes or the plastic walls of the sample vials.

Iron was found to exist in all of the samples and therefore, since most of these samples underwent the cation-exchange process, it is assumed that the NOM binding of iron is significant. If iron remains associated with NOM through the cleaning process, it likely the iron exists as a non-labile species, i.e., a strongly-bound fraction that cannot be removed from NOM matrix by cation-exchange. Only a more rigorous process, like photolysis of metal-ligand bonds, could disrupt these bonds to release iron from the NOM matrix into the bulk solution where it would be free to participate in Fenton chemistry (or any other oxidation process) and to complex OH$^-$ to form photochemically labile species (Fe(OH)$_2^+$, FeOH$^{3+}$). Alternatively, photolysis of Fe(III)-NOM complexes could result in the production of Fe(II)-NOM complexes that may also participate in Fenton chemistry (Voelker and Sulzberger, 1996; Voelker et al., 1997). Either way, the Fe species concerned could behave catalytically to promote the production of the hydroxyl radical. Given that these samples were analyzed for Fe$_T$ well after the experiments were
conducted, it is possible that solutions at the higher pH's "matured" and that the measured levels do not accurately reflect the conditions of the reaction solutions. Reaction solutions were allowed to equilibrate at least 24 hours prior to spiking with alachlor, so it was assumed that iron speciation had equilibrated.

Comparing the reactivity of the SRFA isolate (low iron) solution at a pH of 4.13 to that of the SR raw water (high iron, pH 4.26), the raw water had a $k_{\text{obs}}$ ($0.117 \pm 0.0158 \text{ hr}^{-1}$) almost 6x's greater than that observed for SRFA alone ($0.0199 \pm 0.000882 \text{ hr}^{-1}$). When $k_{\text{obs}}$ is normalized to TOC and corrected for inner filter effects by applying the screening factors measured for the two samples (Table 3.1 and Table 3.5), the factor drops to 2.7 x's. The raw water contained substantially more iron (476 ppb Fe) than the SRFA, yet the difference in reactivity does not reflect a corresponding enhancement. While the data suggests that Fe promotes the reaction, it is unclear how this process occurs.

If iron were promoting the degradation of alachlor, it would most likely do so through the production of the HO* in its participation in the Fenton reaction. Consistent with the trends observed in these experiments, the efficiency of the photo-Fenton reaction was found to increase with a decrease in pH to an optimum value at a pH of 2.8 (Pignatello, 1992). This pH dependency was attributed to the change in speciation of the iron which shifted to favor the photoreactive form (Fe(OH)${}^{2+}$ at the lower pH (Huston and Pignatello, 1999; Pignatello, 1992). Below a pH of 2.8, this species is no longer favored and the reaction rate drops-off again. If iron is at level high enough in natural waters to influence the degradation of a contaminant through the photo-Fenton chemistry, I would expect to see a similar pH dependency for alachlor degradation. The trends observed in
natural waters, however, are expected to deviate from those observed in the clean systems of Pignatello's lab because of the presence of numerous natural water constituents (e.g., natural organic matter, chlorine, sulfate, phosphate) that can complex iron and alter its speciation. Moreover, the effect of some species, such as iron-binding moieties in the natural organic matter matrix, cannot be determined with great certainty. Because the exact nature and strength of iron's association with natural organic matter is not known, it is difficult to estimate what the exactly how much of an effect this will be. Balmer and Sulzberger (1996) examined the various factors that controlled the light-promoted degradation of atrazine in Fe(III)/oxalate systems and found that both the pH and concentration of oxalate significantly affected atrazine degradation. In general, the reaction was promoted at low pH while inhibited at high pH (~8). They attributed the pH effect to its control of iron speciation, which in turn, would affect the reactivity of the iron participating in Fenton pathways. They found that the maximum degradation rate of atrazine was achieved at pH 4 and attributed this to the predominance of the Fe(III)-oxalate complexes Fe(C\(_2\)O\(_4\))\(^{2-}\) and Fe(C\(_2\)O\(_4\))\(^{3-}\). These complexes were presumed to be more photochemically labile than either Fe(C\(_2\)O\(_4\))\(^+\) and Fe(OH)\(^{2+}\). Overall all the role of the organic ligand in this system was presumed to be an electron donor to Fe(III) to form Fe(II) through a LMCT and, in its radical anion form, to react with O\(_2\) to form superoxide which would eventually dismutate to form H\(_2\)O\(_2\). Thus, the literature supports that photo-Fenton pathways involving iron do exhibit pH dependencies similar to what was observed in this study.
The photophysical properties of NOM are known to be pH dependent (Schwarzenbach \textit{et al.}, 1993; Bruccoleri \textit{et al.}, 1993). In general, the measured molar absorptivity of NOM solutions decrease with a decrease in pH, and the absorptivity data presented here is consistent with this behavior (Tables 3.1 and 3.5). Therefore, I would expect that a decrease in pH would inhibit any photochemical process directly resulting from the absorption of light by these NOM chromophores because the probability of NOM absorbing light decreases with a decrease in pH. This interpretation, however, does not provide an explanation that is consistent with the alachlor degradation data: alachlor reacts more readily at a lower pH. Therefore, it would seem a change in the photophysical properties of the NOM is not the primary reason for the observed pH dependency.

Bruccoleri \textit{et al.} (1993), however, determined the quantum yield for intersystem crossing of two well-characterized soil fulvic acids increased with a decrease in pH. Thus, the literature documents at least one photophysical property of NOM that corresponds to my observations for alachlor degradation. The data from the solutions that were argon-sparged, however, argues against involvement of the NOM triplet, unless formation of the triplet is not the rate limiting step to the reaction.

Changes in pH also affect the structural properties of NOM. At constant ionic strength, an increase in the pH causes NOM to become deprotonated which increases the overall polarity of the NOM substrate and decreases the favorability of hydrophobic organic compound partitioning (Schlautman and Morgan, 1993). Earlier studies of the photodegradation of alachlor as promoted by humic substances (Chiron \textit{et al.}, 1995)
placed some emphasis on how partitioning of alachlor into the NOM matrix limits its photodegradation. In that study, however, the authors assert that partitioning of alachlor increased with an increase in pH. They stated that the decrease in reactivity at a higher pH was because partitioning of alachlor to the NOM phase removed it from the reactive pool by reducing its concentration in the bulk solution. The difference in alachlor reactivity between a pH of 7 and 1 was used to determine the fraction of alachlor bound by the humic substances at a high pH (Chiron et al., 1995). This interpretation seems to contradict Schlautman and Morgan’s model and no explanation is provided for Chiron et al.’s interpretation.

I did not consider that the binding of alachlor by NOM would be an important process because alachlor has a relatively high solubility (242 mg/L @ 25°C; MacKay et al., 1995). Calculations based on the reported soil organic carbon partitioning coefficients, $K_{OC} = 170$ L/kg (Gish et al., 1995; Hornsby et al., 1996), showed that no more than 0.2% of the alachlor present in reaction solutions would be associated with the organic matter present in any of the natural waters or NOM isolate solutions tested, assuming that partitioning will not differ significantly between soil and aquatic NOM.

Overall, the data from these experiments support the conclusions that both NOM and iron are mediating the photochemical degradation of alachlor. The effect of the iron is apparently more important at the lower pHs, which is consistent with the idea that the most reactive iron precursors to the hydroxyl radical (various Fe$^{2+}$ species and Fe(OH)$^{2+}$) are stable at the lower pHs. The promotion due to an independent NOM process would be expected to be consistent throughout the pH region studied.
3.3.8 Role of Iron Mediating the Photodegradation of Alachlor

In order to test whether or not there was a possible NOM/Fe synergy, several experiments were performed. In a first set of experiments, iron was "spiked" into SRFA (IHSS isolate) solutions at low (4) and high pH (8). Iron was also spiked into the OWC 9-14-99 RR H+ sample to determine the effect that iron would have in promoting the degradation of alachlor in a natural water sample. Iron was added from a working stock solution of FeCl$_3$•$\text{H}_2\text{O}$ in 1% (v/v) HCl to NOM isolate solutions, H+-saturated natural water, or buffered Milli-Q solutions (control), at a level of 2 µM. Solutions were allowed to equilibrate overnight before adding alachlor. The speciation of the iron was estimated using PHREEQC2.2 (USGS, updated 2000 version) and the known compositions of the solutions. As a crude approximation, the binding of iron by NOM was ignored in these calculations.

The results from these experiments showed several interesting things (Table 3.7; Figure 3.20). First, a difference was observed in the measured rate coefficients for alachlor degradation in the iron control samples (no SRFA) between pH 8 and pH 4 Fe blank (no NOM). The $k_{\text{obs}}$ measured at pH 4 was approximately 5.5$\times$'s higher than that measured at pH 8. Most likely, the cause for the difference in reactivity is caused by the speciation of Fe at these two different pHs. At the high pH, Fe is estimated to exist predominantly (76%) as colloidal (presumably, since a precipitate was not observed in these solutions) Fe(OH)$_3$ (Table 3.8) and to a lesser extent (22%) as Fe(OH)$_4$•$. Only 2% of the Fe is predicted to exist in the photochemically labile form of Fe(OH)$_2^+$ (Kiwi et al.,
With the drop in reactivity at the higher pHs, there is no evidence to suggest that the predominant forms of Fe (Fe(OH)$_3$ and Fe(OH)$_4^{-}$) lead to the degradation of Alachlor.

At the lower pH, however, the speciation of Fe changes. The majority (57%) of the Fe is predicted by PHREEQC2.2 to exist as Fe(OH)$_2^{+}$. Because of the phosphate buffer, FeH$_2$PO$_4^{2-}$ is predicted to be the second most dominant species at 35%. Finally, FeOH$^{2+}$ comprises approximately 8%. Only 0.04% of Fe is estimated to be present as the "free" Fe$^{3+}$ (i.e., Fe(H$_2$O)$_6^{3+}$). It is not clear why the levels of total iron (Table 3.7) differ inconsistently between the high and low pH for both the control and the SRFA/Fe samples; initially, all samples were spiked at the same level of iron. Possible loss of iron from solution at high pH could include precipitation as colloidal iron hydroxides or phosphates. In the absence of detailed pH versus Fe level data for the phosphate buffer control solutions, I would suspect any of the following species, Fe(OH)$_2^{+}$, FeH$_2$PO$_4^{2+}$ and/or FeOH$^{2+}$ to be responsible for the photoreactivity in this solution. Both Fe(OH)$_2^{+}$ and FeOH$^{2+}$ undergo direct photolysis to form the hydroxyl radical, although the reaction is less efficient for Fe(OH)$_2^{+}$ than FeOH$^{2+}$ (Kiwi et al., 2000). FeOH$^{2+}$ has a large molar absorptivity, ~ 2000 M$^{-1}$cm$^{-1}$, at $\lambda = 290$ nm which decreases exponentially to zero at $\lambda = 440$ nm (Faust and Hoigné, 1990). In addition, FeH$_2$PO$_4^{2+}$ complexes are also known to undergo photolysis to form Fe$^{2+}$ and the dihydrogen phosphate radical (Faust, 1994).

While the results from the PHREEQC2.2 calculations indicated that some photochemically reactive inorganic complexes would be expected to form in the control solutions, the results returned by the program did not correspond to the iron speciation that has typically been reported in the literature for solutions of similar composition.
(Faust and Hoigné, 1990; Balmer and Salzberger, 1996). Indeed, Faust and Hoigné, (1990) reported in buffered MilliQ solutions that Fe(Oh)^2+ should be the dominant iron complex at pH 4. Therefore, I suspect the model results are in error and little more was done with the species calculations.

For the SRFA control experiment (no iron added), the alachlor degradation was promoted at a pH of 4 over that at a pH of 8 by a factor of 1.3; however, the given the large error on the pH 8 data, there may not be a statistically significant difference between the two kobs's. The measured iron level was also lower in the pH 4 sample than in the pH 8 sample and, as with the kobs, the error on the iron measurement for the pH 8 sample was also large. Thus, the levels measured at the two pHs may not be statistically different.

SRFA was one of the cleaner (as far as metal contamination) NOM isolates used. The low level of iron measured in this sample corresponded to little difference observed in alachlor reactivity between the high and low pH samples. Thus, it may be expected that the magnitude of the difference observed in alachlor reactivity between a low and high pH will depend on the level of iron. Consistent with this interpretation, the difference in kobs between the high and low pH samples for the SRFA/Fe solution was substantially larger (~ 6 x's) than that (~ 1.3 x's) determined for the SRFA control solution (no iron) (Figure 3.20). Further support for importance of iron comes from the results from the pH studies (Section 3.3.7) in which the sample with the highest iron levels (Fulton Co. water) was promoted at the lower pH to a greater extent than the other samples (SRFA, OWC 9-14-99 RR H+). Taken together, these results suggest that iron plays a role in promoting alachlor degradation at low pH.

171
The $k_{obs}$ for the SRFA/Fe solution at a pH 8 was statistically the same as that observed in the pH 8 SRFA control (no iron) solution. Thus, the addition of almost 25×'s more iron to the SRFA solution had very little effect on the degradation of alachlor at high pH. For both solutions, the $k_{obs}$'s were three times higher than that observed for the iron control (no SRFA) solution. This result suggests that iron has very little role in influencing the degradation of alachlor in the SRFA solutions at the high pH and that the reaction must be promoted predominately by the SRFA.

The results from the iron control (no NOM) experiment showed that iron photochemistry may account for about 35% of the reaction (SRFA/Fe) at the higher pH since the iron speciation was estimated to be distributed among the same species the two solutions at nearly the same concentrations based upon the PHREEQC modeling (Table 3.8). But, again, this interpretation is doubtful because the PHREEQC2.2 modeling did not take into account the formation of NOM-iron complexes which should bind a substantial fraction of the iron, especially at high pH. Therefore, the reactivity observed in the control solutions may arise from completely different iron species than those in the NOM solutions, depending on what the magnitude of the equilibrium coefficients are for Fe-SRFA complexes. If I make the assumption that iron is completely bound by the NOM at high pH in photochemically unreactive complexes, then the degradation of alachlor in the high pH SRFA solutions could be completely attributed to photochemical intermediates generated from the NOM itself. This would explain why the $k_{obs}$ of the iron amended SRFA solution at high pH was virtually the same as that measured for the SRFA control solution. Alternatively, if Fe(III)-NOM complexes do undergo photolysis to form
Fe$^{2+}$ at high pH, oxidation of the generated Fe$^{2+}$ species by oxygen (Voelker et al., 1997; King, 1998) or even superoxide (also produced photochemically) (Emmenegger et al., 2001) is expected to be quite rapid. Since O$_2$ concentration in air-saturated solutions approaches $\sim 250 \mu$M, it could outcompete H$_2$O$_2$ for Fe$^{2+}$ thereby shutting-off the Fenton pathway.

At the lower pH, $k_{obs}$ for the iron amended SRFA solution increases substantially: it was over 4.5 times greater than that observed in the SRFA control (no iron). There was ten times more iron present in the amended solution than in the SRFA control and again, if iron promoted the reaction, a dramatic increase in the alachlor degradation should have been observed. If I assume that alachlor degradation arises from two, independent, pseudo-first order processes, i.e., one from the NOM and one from the iron, then the $k_{obs}$ measured for the iron amended SRFA solution should be equal to the sum of the contributions from the two sources, i.e., $k_{obs} = k_{NOM} + k_{Fe}$. Each control experiment (Fe and SRFA alone) can be considered a measurement of the respective independent processes, and, assuming the gravimetric amount of iron added to all solutions was the same, the measured rate coefficients can be added to produce a predicted $k_{obs}$ for the combined (SRFA/Fe) solution. The results (cross-hatched bars) from these calculations are presented (Figure 3.20). At pH 8, the sum, given the error, is not statistically different from that measured in the SRFA and the SRFA/iron solution (propagation of error bars not shown). Again, this indicates that Fe is probably playing a very minor role at this pH.
At the low pH, however, the actual $k_{obs}$ is significantly larger (46%) than the simple sum (0.0459 hr$^{-1}$) of the $k_{obs}$'s from the SRFA and iron controls and suggests that a third mechanism that involves a synergistic relationship between the SRFA and iron to produce hydroxyl radicals may be occurring in addition to the other two mechanisms.

Even if the $k_{obs}$ for the iron control is "corrected" by normalizing $k_{obs}$ to the iron level and then multiplying by the level measured in the iron amended solution, the sum still falls short (by 15%) of accounting for the $k_{obs}$ in the Fe amended solution. Moreover, in adding these rate coefficients, I have NOT corrected for the scavenging or inner filter effects that the NOM would have on the reaction for these experiments, assuming that HO$^*$ is the reactive species. If these considerations were included, the predicted $k_{obs}$ should decrease the calculated sum even further.

Alternatively, White (2000) tested these same samples for the production of HO$^*$ using the MeOH scavenging method (Zhou and Mopper, 1990). The iron control, SRFA control, and SRFA/Fe samples produced HO$^*$ at the rates of 0.11, 3.0, $10 \times 10^{-10}$ M HO$^*/s$, respectively, for this photoreactor. Thus, SRFA/Fe sample had a HO$^*$ production rate some 90x's greater (or 45 x's when corrected for differences in iron levels) than the Fe control, and only 3.5x's greater than the SRFA control. Given these production rates and the published rate coefficient for the scavenging of hydroxyl radical by SRFA ($3.1 \times 10^4$ mgC/L$^{-1}$s$^{-1}$; Westerhoff et al., 1999), I would expect a predicted $k_{obs}$ for the solutions of 0.0198, 0.0225, and 0.0765 hr$^{-1}$ assuming that alachlor is only reacting with the HO$^*$. For the SRFA control, the predicted rate coefficient (0.0225 hr$^{-1}$) completely accounts for
the $k_{obs}$ (0.0224 hr$^{-1}$) within experimental error. For the iron control and the SRFA/Fe solution, however, the predicted rate coefficients underestimate $k_{obs}$ by 40% for the Fe control and 25% for the SRFA/Fe solutions.

A possible explanation for this underprediction is that alachlor may bind to iron to form a photolabile complex which would increase alachlor reactivity in the iron control. One could envision that alachlor could react as a bidentate chelator, assuming that the lone pair of electrons from either oxygen and lone pair off the carbonyl on the chlorinated side chain can donate electrons to Fe$^{3+}$ to form the bonds. Theoretically, a six-membered ring would form, which would be sterically favorable. The complexation of iron by alachlor would be expected to diminish in the presence of the SRFA because of competition from NOM ligands. Such an explanation is also consistent with some of the observations in the raw water experiments (Section 3.3.2) that contained high levels of iron. For example, for the high nitrate containing OWC 6-29-98 IN sample, which also contained a high level of iron, the predicted rate coefficients based upon reported HO$^\bullet$ production rates from the raw water underpredicted the $k_{obs}$ at a low pH whereas at the high pH, the predicted rate coefficient was able to account for 103% of the $k_{obs}$. If this mechanism occurs, then a non-linear relationship would be expected to exist between iron level and measured $k_{obs}$ due to the complexation equilibrium. Later in this study (Section 3.3.9), I present data that shows up to 50 ppb iron (0.9 µM) (Figure 3.23), the relationship between the two is linear which would not support an alachlor binding mechanism.

Another explanation for these discrepancies could be that these calculations fail to take into consideration other complexes (e.g., iron-phosphate) that may form and
influence the reaction of alachlor. For example, iron-phosphate complexes could photolyze to form Fe(II) and phosphate radicals (Faust, 1994). If the phosphate radicals react with the alachlor, this could produce a $k_{\text{obs}}$ that exceeds $k_{\text{pred}}$. Additionally, as a result of photolysis, Fe(III) is reduced to Fe(II). It was not tested in these experiments if Fe(II) reduces alachlor, although I would not expect MeOH to quench this reaction pathway.

The results obtained for the iron amended experiments with the OWC 9-14-99 RR H+ water are consistent with SRFA solutions (Figure 3.21). In order to compare results between the raw and H+ water, rate coefficients were normalized to the amount of organic carbon present. At the high pH, the measured degradation rate coefficients were fairly low, but it appears the H+ saturated water reacted 4.3×'s faster than the raw water. (Recall that at pH's above 6, the $k_{\text{obs}}$ were statistically the same and so, I compare the pH 8.00 and pH 7.66 sample with equal weight.) For the pH 4 samples, the H+ saturated water had less reactivity toward alachlor degradation than the raw water (by 1.3×’s) and was expected based upon the results from the SRFA experiments (less iron, less reactivity). The cation-exchange process removed approximately 91% of the iron present in this sample according to the measured iron data in Table 3.7, and if iron were promoting the process, its removal should inhibit the process.

Differences in the measured TOC levels may explain in part some of the differences observed for alachlor reactivity in the OWC 9-14-99 RR samples. Since the NOM will affect both scavenging and production of reactive transients, the higher level of TOC in the raw water may enhance its scavenging role more significantly than its reactive
radical production role for the high pH samples. While this could explain the high pH data, it fails to explain the low pH data.

The differences in reactivity between the raw and H+ saturated OWC 9-14-99 sample may also result from changes in the photochemical properties of the NOM due to loss of photoreactive moieties on the cation-exchange process. When the raw water was passed through the cation-exchange column, NOM was removed from the water in addition to the labile metals resulting in a change in the NOM chromophores. Indeed, the normalized (to the amount of carbon) extinction (ε) at 280 nm goes from 228 M⁻¹cm⁻¹ in the raw water (Table 3.1) at pH 8 to > 257 M⁻¹cm⁻¹ for the H+ saturated solution (Table 3.5). The same trend is observed for the samples at a pH of 4: the measured molar extinction increases from 216 M⁻¹cm⁻¹ in the raw water to 231 M⁻¹cm⁻¹ in the H+ saturated water. This increase in absorptivity may result in a more efficient photochemical production of reactive intermediates in H+ saturated water.

An increase in photochemical reactivity should occur at high pH rather than at low pH. If functional groups involved in metal complexation, such as carboxyls (a carbonyl can undergo a π-π* transition) are no longer bound to unreactive metals (such as calcium), their "free" electrons are prone to electronic transition. Once protonated (by lowering the pH), however, the probability of absorption will be diminished (if not diminished, then at least would undergo a hypsochromic shift) and thus, appear to lower molar extinctions at a given wavelength (Table 3.5). The greater reactivity of the H+ water than the raw water at the high pH is consistent with the interpretation that free carboxyls will be more photochemical reactive. Thus, this observation suggests that
NOM is the primary source of reactive intermediates at high pH. At low pH, however, protonation would inhibit the photochemical transition, and therefore, this effect may not be so noticeable. I would expect differences in alachlor reaction to result from another factor, like the difference in measured iron levels.

Moreover, the experiments preformed with the H+ saturated water at low pH also suggested that either very little iron is necessary to promote the reaction or that other water constituents besides iron are promoting these processes. I removed 91% of Fe through cation-exchange and only saw around 39% reduction in measured \( k_{\text{obs}} \) from the raw water. The fact that I did not see a corresponding decrease in \( k_{\text{obs}} \) to the amount of Fe removed suggests that metals are highly catalytic and only a small amount is necessary to drive the reaction, and/or that metals are not solely responsible for the observed degradation. If the latter case is true, then another water constituent is also promoting these processes to a significant extent when the iron levels are low. Based upon the previous results, I would assume this constituent to be the NOM.

When the OWC 9-14-99 RR H+ water was amended with iron (at 2 \( \mu \text{M} \)) at pH 4, (no experiment was performed at a pH of 8 due to the fact I had depleted the sample), \( k_{\text{obs}} \) was dramatically promoted (6.5 \( \times \)'s) (Figure 3.21). Performing similar calculations as for the SRFA solution, the sum of the rate coefficients measured for the OWC 9-14-99 RR H+ and iron controls at pH 4 accounted for only 34% of the \( k_{\text{obs}} \) of the iron amended solution. Even normalizing \( k_{\text{obs}} \) to the measured Fe level did not account for the level of promotion: the "corrected" sum accounted for only 44% of the \( k_{\text{obs}} \) of the amended solution. This experiment provides further evidence that the iron and most likely, the
NOM are reacting synergistically to provide a third mechanism leading to the degradation of alachlor. In examining how humic substances affected iron cycling, Voelker et al. (1995) found the presence of organic matter promoted the reduction of Fe$^{3+}$ to Fe$^{2+}$ in the light. At low pHs, Fe$^{2+}$ was more stable because rate of oxygen oxidation was relatively slow compared to the rate of oxidation at high pHs.

If the NOM is also producing H$_2$O$_2$ through an alternative processes, then a situation is created where photo-Fenton chemistry could be quite efficient in producing the hydroxyl radical. The measured H$_2$O$_2$ production in the OWC 9-14-99 RR water (Section 3.3.5) provides support that Fenton chemistry is occurring in the OWC waters. Because Fe$^{2+}$ species are efficiently oxidized by O$_2$ at high pH, the H$_2$O$_2$ accumulation will occur until it reaches a steady-state concentration. At low pH, H$_2$O$_2$ never attains a significant level indicating that it is efficiently reacting through some other process (i.e., Fe$^{2+}$). Again, this is a simplistic interpretation. Certainly the kinetics of ROS reactions are driven by their redox properties as well as by the pH.

There are, however, a couple of caveats. It is also possible that another anion, such as sulfate, may complex with the iron and react in the raw water in contrast with the "clean" SRFA solutions. This may explain why the promotion was more extensive for the raw water. The predominant sulfate complex of Fe was predicted by PHREEQC to bind < 1% of the Fe (Table 3.8), and therefore, its effect would be minimal.

Iron is also distributed differently in the OWC 9-14-99 RR H+ water as compared to the SRFA solutions. In the OWC 9-14-99 RR H+ water, 88-89% of the Fe is predicted to exist as Fe(OH)$_2^+$ while another 11% as FeOH$^{+2}$ (Table 3.8). Part of the reason for the
difference is because these solutions did not contain a phosphate buffer, which is predicted to bind a substantial amount of Fe in the SRFA solutions. Although these calculations do not consider the effect of binding by the NOM, differences in speciation due to differences in solution composition are expected to be significant. It is possible that iron could exist in a more photochemically labile form in the OWC water than in the SRFA solutions. This consideration makes $k_{\text{prod}}$ (based upon taking the sum of the iron and water sample controls), a little more tentative, because 35% of the iron in the control was tied up as FeH$_2$PO$_4$ which would be "free" in the OWC 9-14-99 RR water solutions.

This idea presents an interpretation that is consistent with the data. The SRFA control and the OWC 9-14-99 RR H+ contained almost the same amount of TOC and their $k_{\text{obs}}$ are statistically indistinguishable. However, when the iron is added, alachlor reacted 42% slower in the SRFA solution, even though it contained more iron (by measurement) than the OWC 9-14-99 RR H+ water. Complexation of a significant fraction of the iron by phosphate may be the cause for the "depression" in alachlor reactivity in the SRFA solutions, if these complexes are unreactive, or form colloidal precipitates. Alternatively, complexation by organic ligands in the NOM may also depress the reaction. SRFA may complex iron to a greater extent than the NOM present in the OWC 9-14-99 RR H+ leading to non-productive (from a photochemical standpoint) processes and less alachlor degradation.

In these preliminary experiments, the addition of iron was found to significantly increase the rate of reaction for alachlor degradation. Additionally, NOM was found to be important in mediating these processes either through the production transient precursors
(like \( \text{H}_2\text{O}_2 \)) or reactive transients that react with alachlor. Since iron was found to induce a reaction, the role of NOM in mediating these reactions cannot be assessed until the extent that iron can influence the reaction is determined. While the iron level in the NOM control solutions was extremely low, was it enough to induce reactions? Most researchers have dismissed such NOM samples as being “clean” (or metal-free) and, in these cases, the role of trace amounts of iron in promoting photochemical processes is neglected.

3.3.9 Limits on the Effect of Iron on the Degradation of Alachlor in IHSS NOM Standard Solutions

Iron was found to play a role in alachlor degradation, although the extent of its influence was not well-defined. To summarize, there have been several mechanisms discussed that could mediate to alachlor degradation: (1) the production of the \( \text{HO}^\bullet \) from the direct photolysis of the NOM; (2) the production of the \( \text{HO}^\bullet \) from the direct photolysis of “free” iron species (iron hydroxides); (3) the production of \( \text{HO}^\bullet \) through the synergistic interaction of NOM with iron (\textit{i.e.}, photo-Fenton chemistry); (4) the formation of alachlor-Fe complexes that are photolabile resulting in the reduction of \( \text{Fe}^{3+} \) and the oxidation of alachlor; (5) the production of radicals (such as the phosphate radical) from the photolysis of inorganic iron complexes that can react with alachlor. The following set of experiments were performed to establish the minimum concentration of iron necessary to produce an observable effect in promoting the degradation of alachlor and to
investigate the possibility that NOM behaves synergistically with iron to affect alachlor degradation.

In order to study the effect of NOM, two types of USGS NOM standard isolates were chosen for study: SRFA and LFFA. These NOMs differ substantially from one another due to their source. The SRFA is derived primarily from terrestrial (plant/soil) sources (allochthonous) whereas the LFFA originates from microbial or algal sources (autochthonous). Due to the contribution of lignin, terrestrial sources of NOM are generally more aromatic with higher C:N ratios (McKnight and Aiken, 1998) compared to microbial/algal sources. The samples chosen here represent the two compositional extremes (so called, "end-members"). As a result, I would expect the two NOMs to behave differently in their ability to complex iron and in their photochemical properties. Thus, differences should be observed in regards to their mediation of alachlor degradation.

In order to ensure that reactive pathways with these NOMs would be similar to those observed in the natural waters samples, a few control experiments were performed (Figure 3.22). First, alachlor was irradiated in buffered (pH = 3.6) MilliQ, SRFA (8 mgC/L), LFFA (8 mgC/L), and LFFA (8 mgC/L) + iron (25.49 ± 0.46 ppb Fe) (dark bars). A split of these solutions (except for the buffered MilliQ) were spiked with MeOH (0.05 M) and also irradiated. The results were consistent with what was observed in the natural waters. Alachlor showed no reactivity in the dark controls (data not shown). The presence of NOM (any NOM) significantly enhanced the light reaction from that observed in the buffered MilliQ water experiment. When iron was added to the solution,
the rate coefficient was promoted to a greater extent. In the presence of MeOH, there was no statistically significant degradation of alachlor in any of the solutions, indicating that the hydroxyl radical pathway is the predominant pathway leading to alachlor degradation. Given the error associated with the LFFA solution, a judgment cannot yet be made as to which of the two NOMs are more reactive toward alachlor degradation.

In a second series of experiments, a stock solution of each NOM containing the same TOC was made in phosphate buffered MilliQ Water (5 mM; pH 3.6). These solutions were divided into 8, equal-volume portions. An aliquot of Fe (III) (from an acidified (0.01 M H₂SO₄, (trace metal grade) stock solution of FeCl₃·6H₂O) was added to each split resulting in a series of solutions that contained iron in the range of 0-50 ppb. Volume differences were made up by the addition of buffer so that each solution had the same final volume and concentrations of TOC (8.05 ± 0.11 mg-C/L for SRFA and 8.11 ± 0.09 mg-C/L for LFFA) and buffer (5 mM phosphate) (Table 3.9). As a control, an experiment was also carried out in a buffered (5 mM phosphate) MilliQ water solution containing only iron.

All plots of the data fit the pseudo-first order kinetic model reasonably well ($R^2 > 0.99$). The dark reaction was found to be statistically insignificant during the course of the experiments (25 hours) (Table 3.9). In all solutions, the photochemical promotion of the degradation of alachlor was observed in comparison to results from the phosphate buffer blank experiment (i.e., buffered MilliQ without any iron added).

In order to assess how low levels of iron influenced the photochemical reaction, rate coefficients observed were plotted versus the corresponding iron level for a given
solution (Figure 3.23). These plots revealed some interesting trends. First, the iron control showed that $k_{obs}$ was correlated ($R^2 = 0.98$) to the amount of Fe$_T$. The data suggests that low levels of Fe (< 3 ppb) are enough to facilitate a photochemical degradation reaction of alachlor in the absence of the NOM, and is consistent with the iron control experiment containing a high level of iron. Unfortunately, the lower limit for promotion of the reaction by iron alone could not be determined from this experiment. The lowest level of iron that could be achieved in a solution under our laboratory conditions (i.e., trace contamination from buffers and reagents used) was 2.94 ppb Fe$_T$.

Even though the plot appears to suggest that iron will not be important below the level of iron determined from the X-intercept (2.78 ppb Fe$_T$) of the extrapolated line, a conclusion cannot be definitively made given the error of this data set. A study conducted using even lower concentrations of Fe would have to be performed.

The curves generated from the results with the NOM solutions fell above the iron control line at low Fe$_T$ levels and below the iron control line at the higher Fe$_T$ levels (Figure 3.23). Both SRFA and LFFA facilitated the reaction in a way that is directly proportional to Fe$_T$ at the lowest Fe$_T$ levels, but at the higher Fe$_T$ levels, the rate of increase of $k_{obs}$ with Fe$_T$ levels-off. In addition, at the higher Fe$_T$ levels, the SRFA and LFFA curves diverge whereby SRFA/Fe solution was the more reactive of the two solutions. It would appear that at the higher levels of the iron range studied here, the dominant role of the NOM switches from promoting the reaction to quenching the reaction. The extent that NOM influences the reaction is apparently dependent on the composition of the NOM.
The difference observed between the two NOM solutions is rather surprising. As far as quenching, SRFA is reported to only a slightly (~5%) better scavenger of hydroxyl radicals than LFFA (Westerhoff et al., 1999). Thus, if scavenging reactions were driving the quenching, I would have expected to see overlap of the two curves because of their similar 2\textsuperscript{nd} order scavenging rate coefficients would yield similar calculated NOM scavenging rates for both solutions. The divergent trend for alachlor degradation in the two NOM solutions suggests that a mechanism other than scavenging is the causing the quenching.

The SRFA solution was more colored when compared to the LFFA. The SRFA consistently has a higher molar absorptivity than the LFFA solution (Figure 3.24) which is consistent with the observation that allochthonous NOM typically has a higher absorptivities than autochthonous NOM (Donahue et al., 1998). Thus, I expected the SRFA solutions to be more reactive than the LFFA solutions considering only consider NOM promoted processes. In order to evaluate the effect of SRFA and LFFA on promoting the degradation of alachlor in the absence of iron, the linear regions of the $k_{\text{obs}}$ vs Fe\textsubscript{Total} plots were extrapolated to obtain a value for the y-intercept (Figure 3.25 a, b). This value provides an estimate of the expected $k_{\text{obs}}$ at a theoretical 0 ppb Fe\textsubscript{Total} level (This assumes that a linear relationship is obeyed at very low Fe\textsubscript{T}). LFFA had a larger intercept (0.0140 hr\textsuperscript{-1}) than the SRFA (0.0103 hr\textsuperscript{-1}), which could be interpreted to mean that LFFA is more reactive than SRFA toward promoting alachlor degradation in the absence of Fe which is counter intuitive to the measured photochemical properties of each NOM. Considering the error associated with the measurement, the differences in the
intercepts are probably not statistically different. In addition, the data from White (2000) indicate that the production of HO· is greater per mg C/L from SRFA than LFFA. White (2000), however, did not take into consideration the effects that trace levels of iron may have in promoting the reactions. In White's experiments, the SRFA solution contained 5.76 ppb Fe_{Total} while the LFFA acid contained 0.62 ppb Fe_{T}. When these levels of iron are taken into consideration, \( k_{pred} \) accounts for 112% and 105% of \( k_{obs} \) for these experiments at the comparable iron level.

In the presence of the iron, however, it appears that SRFA solution is the more reactive of the two NOM solutions because the slope of the extrapolated line for the SRFA is twice that of LFFA. Both slopes are still lower than the slope of the iron control line corroborating NOM's role as both a producer and scavenger of HO·. The smaller slope of the LFFA sample indicated that LFFA is a better quencher of the reaction than SRFA. Inner filter effects from NOM attenuation must play a minor role because the LFFA solutions were less reactive even though their screening factors were smaller (Table 3.9).

The production and quenching of HO· must arise from an interaction that the NOM has with the iron. For the moment, if I consider that two independent, pseudo-first order processes leading to the photochemical degradation of alachlor are occurring, one from the NOM and one from the Fe, then a predicted rate coefficient can be derived for each iron level by summing the contribution to the degradation rate coefficient from the DOM alone (i.e., the intercept from the extrapolated DOM curve) and the contribution
from the iron promoted process (determined from the linear regression line from the iron control experiment). Thus,

\[
k_{\text{pred}} = (0.0103 \text{ or } 0.0140) \text{ hr}^{-1} + ((0.00138 \times [\text{Fe}_{\text{Total}}](\text{ppb})) - 0.00393) \text{ hr}^{-1}
\] (3.23)

The calculation was performed for both the SRFA and LFFA solutions and plotted to compare to the actual observed rate coefficient (Figure 3.26). At the lower Fe levels, the \(k_{\text{pred}}\) adequately predicts \(k_{\text{obs}}\). As the level of iron increases, the predicted value exceeds the value actually observed for both NOMs, i.e., the extent of the difference between \(k_{\text{pred}}\) and \(k_{\text{obs}}\) increases with increasing iron level. These results contradict the results from the experiments conducted at higher levels (>100 ppb or ~ 2 \(\mu\)M) of iron. In that experiment, the \(k_{\text{obs}}\)'s for the SRFA+Fe solution and for the H+ saturated natural water + Fe solution were higher than that predicted from the simple sum of rate coefficients observed for the NOM (natural water) and iron controls. The reason for this discrepancy is not understood.

There are several explanations that could explain the observed inhibition in the low-level iron experiments. (1) NOM binds Fe\(^{3+}\) in a photochemically unreactive complex; (2) at such low iron concentration, there is insufficient iron to compete with other ligands present (phosphate, sulfate, OH\(^-\)); (3) NOM complexation of Fe\(^{2+}\) inhibits the Fenton cycle, or, reacts directly with Fe\(^{2+}\) in a process that competes with reaction of Fe\(^{2+}\) with H\(_2\)O\(_2\); (4) at higher Fe\(^{3+}\) levels, it complexes with photoreactive sites on the NOM (e.g., carbonyls in quinone moieties) to block the production of HO\(^*\) (i.e., Fe shuts down the direct photolysis of the NOM); (5) there are only a limited number of
photoreactive binding sites in the NOM; (6) formation of iron polymers or precipitates is more important in removing iron from the reactive matrix; (7) the formation of iron precipitates creates a surface that preferentially sorbs photoreactive NOM moieties (Meier et al., 1999). The only argument I have against scenario (4) is the results from the OWC 9-14-99 RR water. If Fe (or other metals) blocked reactive NOM sites, then I would have expected the OWC 9-14-99 RR H+ water to have a higher reactivity than the raw water at a low pH. Instead, the normalized (to the TOC) $k_{obs}$ for the raw water was higher (3.94 hr$^{-1}$ L/mgC) than that for the H+ saturated water (3.02 hr$^{-1}$ L/mgC).

Inorganic species added to the solutions from the buffer and acid adjustment may also have affected the reactions. The final concentration of sulfate in the reaction solutions was 2x10$^{-4}$ M. The concentration of the phosphate buffer was 5.0x10$^{-3}$ M and the pH was 3.6. The fact that these species can bind Fe significantly may prove to alter the conditions of the reaction solutions. Iron may also be forming unreactive phosphate precipitates (Stumm and Morgan, 1981). Hug et al. (1997) states that the presence of a strong binding ligand for Fe$^{3+}$ would lower the $pE$ of a solution and shift equilibrium toward Fe$^{2+}$; therefore Fe$^{2+}$ would be a stronger reductant and more likely to react with O$_2$ or H$_2$O$_2$ to form the hydroxyl radical. Fe$^{2+}$ can also form a charge transfer complex with the SO$_4^{2-}$ which absorbs light in the 300 nm region (Faust, 1994). In this reaction, Fe$^{2+}$ transfers an electron (MLCT) to the sulfate forming sulfate radicals and Fe$^{3+}$.

Because sulfate was at a consistent concentration for each experiment, however, the effect on all reactions should be the same, and the observed general trends should still hold.
This work showed that low levels of iron (~2 ppb or 25 nM) can catalyze the transformation of alachlor at realistic levels of NOM and that this reaction can be quenched at higher levels of iron by the NOM. Therefore, caution must be used with using “clean” NOM standards to study photosensitization processes. Even trace contamination iron from sources such as "metal-free" acids may be promoting, in part, the observed photosensitization. One of the more interesting aspects to this study was the difference in reactivity observed between the SRFA and LFFA solutions.

3.4 Conclusions

Indirect photolytic pathways were found to be more significant in the photodegradation of alachlor in pH-adjusted wetland surface water samples than at ambient pH levels. The experimental evidence suggested that alachlor degradation was caused by its reaction with HO•. Analysis of water samples revealed three primary constituents that would promote production of the HO•: nitrate, dissolved natural organic matter (NOM), and iron. For both pHs, the extent of the observed indirect photolysis pathway due to nitrate appears to be dependent upon the concentration of nitrates and the presence of HO• scavengers such as dissolved NOM and carbonate species. Because of the level of TOC measured in these samples, it was a primary scavenger of the HO• in the tested samples. Carbonate species are expected to play an insignificant role in scavenging for these natural waters. During conditions of low concentrations nitrate (<50 uM), NOM becomes the principal photosensitizer at a high pH either through the production of
HO• and/or production of an unidentified transient species. At high pH, NOM and/or nitrate may play a role in the indirect photolysis of non-point source pollutants passing through wetland waters.

Probably most interesting was the effect that pH had in influencing the extent of the indirect photolysis pathways for all samples tested: at lower pH's, indirect processes were significantly enhanced. Nitrate was no longer the principle precursor. Instead, alachlor degradation was promoted primarily by the induction of a trace metal pathway involving NOM. When further probed, low levels of iron (< 5 ppb) promoted alachlor degradation significantly. At very low levels of iron the rate coefficient for alachlor degradation was greater in the presence of NOM. Alachlor was degraded to a greater extent in the SRFA solutions than in LFFA solutions. Thus, the promotion of alachlor degradation by trace levels of iron depended upon the presence and type of NOM. Once, however, the iron level was increased beyond a certain level (different for each type of NOM), the dominant effect of the NOM was to quench the reaction. The reason for this behavior cannot be adequately assessed from the data set presented and needs further investigation.
<table>
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<th>Sample</th>
<th>pH</th>
<th>TOC (mg C/L)</th>
<th>ε  (M⁻¹ cm⁻¹)</th>
<th>Σ S (µg/L)</th>
<th>Nitrate (mM)</th>
<th>Fe⁺⁺⁺ (M)</th>
<th>Alkalinity (mM as CaCO₃)</th>
<th>k₉₅ (hr⁻¹)</th>
<th>pH₄: pH₃⁹²²</th>
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<td>100</td>
<td>0.92</td>
<td>0.0085</td>
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<td>56.99 ± 1.13</td>
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</tbody>
</table>

1 Measured pH of experimental solution  2 Phosphate buffer (5 mM)  3 Where ± values are one standard deviation for replicate samples  4 NR: not reported; values not statistically different from zero  5 Molar absorbivity (normalized for carbon and corrected for nitrate absorption) at λ = 280 and 320 nm  6 NA: not applicable  7 Light screening factor calculated for λ's 290-375 nm  8 ND not detected  9 The values for k₉₅ (corrected for variation in lamp intensity) are reported ± 95% CI  10 Factor that reaction was promoted by pH adjustment  11 NA: not applicable; at least one of the k₉₅ was statistically zero

Table 3.1: Water quality characteristics and measured rate coefficients for alachlor degradation in the natural water samples.
<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>TOC</th>
<th>( \varepsilon ) (M(^{-1})cm(^{-1}))</th>
<th>( \Sigma_{\text{Spec.}} )</th>
<th>Nitrate</th>
<th>( \text{Fe}_{\text{Total}} )</th>
<th>( k_{\text{obs}} \times 10^3 )</th>
<th>( k_{\text{obs}} \cdot \text{TOC} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>OWC 9-14-99 RR</td>
<td>8.00</td>
<td>11.03 ± 0.03</td>
<td>228</td>
<td>100</td>
<td>0.92</td>
<td>0.0085</td>
<td>10.00 ± 0.37</td>
<td>2.97 ± 1.11</td>
</tr>
<tr>
<td>OWC 9-14-99 RR</td>
<td>4.08</td>
<td>11.33 ± 0.15</td>
<td>216</td>
<td>92</td>
<td>0.92</td>
<td>0.0085</td>
<td>12.53 ± 0.07</td>
<td>44.7 ± 5.4</td>
</tr>
<tr>
<td>OWC 9-14-99 RR Argon Sparged</td>
<td>4.08</td>
<td>11.33 ± 0.15</td>
<td>223</td>
<td>95</td>
<td>0.89</td>
<td>0.0085</td>
<td>12.53 ± 0.07</td>
<td>27.4 ± 5.6</td>
</tr>
<tr>
<td>OWC 9-14-99 RR w/ MeOH</td>
<td>4.07</td>
<td>NR (^4)</td>
<td>213</td>
<td>92</td>
<td>0.91</td>
<td>0.0085</td>
<td>12.53 ± 0.07</td>
<td>NR (^4)</td>
</tr>
<tr>
<td>OWC 9-14-99 RR w/ Catalase</td>
<td>4.08</td>
<td>NR (^4)</td>
<td>NR (^4)</td>
<td>NR (^4)</td>
<td>NR (^4)</td>
<td>NR (^4)</td>
<td>41.0 ± 2.9</td>
<td>0.00362</td>
</tr>
<tr>
<td>OWC 9-14-99 RR H(^+) Saturated</td>
<td>7.66</td>
<td>NR (^4)</td>
<td>NR (^4)</td>
<td>NR (^4)</td>
<td>NR (^4)</td>
<td>NR (^4)</td>
<td>2.74 ± 6.45</td>
<td>11.3 ± 2.3</td>
</tr>
<tr>
<td>OWC 9-14-99 RR H(^+) Saturated</td>
<td>4.14</td>
<td>9.06 ± 0.04</td>
<td>231</td>
<td>95</td>
<td>0.99</td>
<td>0.0085</td>
<td>1.12 ± 0.12</td>
<td>27.4 ± 4.6</td>
</tr>
<tr>
<td>Fulton Co. UF Isolate (^3)</td>
<td>4.08</td>
<td>3.49 ± 0.04</td>
<td>250</td>
<td>129</td>
<td>0.97</td>
<td>0.00304</td>
<td>33.70 ± 0.23</td>
<td>45.9 ± 7.0</td>
</tr>
<tr>
<td>Fulton Co. UF Isolate (Argon Sparged) (^3)</td>
<td>4.08</td>
<td>3.49 ± 0.04</td>
<td>250</td>
<td>129</td>
<td>0.97</td>
<td>0.00304</td>
<td>33.70 ± 0.23</td>
<td>27.2 ± 8.1</td>
</tr>
</tbody>
</table>

1 Measured pH of experimental solution  
2 Phosphate buffer (5mM)  
3 Where ± values are one standard deviation for replicate samples  
4 NR: not reported; values not statistically different from zero  
5 Molar absorptivity (normalized for carbon and corrected for nitrate absorption) at \( \lambda = 280 \) and 320 nm  
6 Light screening factor calculated for \( \lambda 's \) 290-375 nm  
7 The values for \( k_{\text{obs}} \) (corrected for variation in lamp intensity) are reported ± 95% CI  
8 Values of \( k_{obs} \) were normalized to the DOC.

Table 3.2: Experimental results used to determine the reactive phototransient responsible for alachlor degradation.
<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>TOC (mgC/L)</th>
<th>$e^4(M^{-1}cm^{-1})$</th>
<th>$\Sigma S_{290-375}$</th>
<th>Fe$_{Total}$</th>
<th>$H_2PO_4^{−}_{Total}$</th>
<th>SO$<em>4^{2−}</em>{Total}$</th>
<th>$k_{obs} \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OWC XAD-8 Isolate$^2$</td>
<td>4.08</td>
<td>2.26 ± 0.05</td>
<td>348</td>
<td>170</td>
<td>0.97</td>
<td>0.76 ± 0.09</td>
<td>5.10</td>
<td>0.00</td>
</tr>
<tr>
<td>4.06</td>
<td>4.33 ± 0.04</td>
<td>323</td>
<td>167</td>
<td>0.99</td>
<td>1.51 ± 1.31</td>
<td>4.84</td>
<td>0.3375</td>
<td>20.3 ± 0.7</td>
</tr>
<tr>
<td>4.05</td>
<td>6.20 ± 0.07</td>
<td>327</td>
<td>167</td>
<td>0.91</td>
<td>2.37 ± 0.13</td>
<td>5.10</td>
<td>0.0900</td>
<td>25.3 ± 1.0</td>
</tr>
<tr>
<td>4.09</td>
<td>8.33 ± 0.08</td>
<td>322</td>
<td>165</td>
<td>0.89</td>
<td>1.33 ± 0.59</td>
<td>5.09</td>
<td>0.1125</td>
<td>32.0 ± 1.4</td>
</tr>
<tr>
<td>4.08</td>
<td>9.20 ± 0.01</td>
<td>326</td>
<td>166</td>
<td>0.85</td>
<td>0.82 ± 0.43</td>
<td>5.00</td>
<td>0.0179</td>
<td>29.2 ± 1.8</td>
</tr>
<tr>
<td>4.08</td>
<td>13.08 ± 0.02</td>
<td>320</td>
<td>164</td>
<td>0.83</td>
<td>5.34 ± 2.43</td>
<td>5.07</td>
<td>0.00</td>
<td>34.9 ± 1.9</td>
</tr>
</tbody>
</table>

1 Measured pH of experimental solution  
2 Phosphate buffer (5mM)  
3 Where ± values are one standard deviation for replicate samples  
4 Molar absorptivity (normalized to carbon) at $\lambda = 280$ and 320 nm.  
5 Light screening factor calculated for $\lambda$'s 290-375 nm  
6 The values for $k_{obs}$ (corrected for variation in lamp intensity) are reported ± 95% CI

Table 3.3: Water quality characteristics and measured rate coefficients for alachlor degradation in the natural organic matter isolate (XAD-8 extract) of Old Woman Creek.
Sample | $R_{\text{prod}}$ (M HO⁻/s) | $R_{\text{prod}}$ (M HO⁻/s) due to H₂O₂ photolysis | % of $R_{\text{Total}}$ | $k_{\text{obs}} \times 10^3$
--- | --- | --- | --- | ---
OWC XAD-8 Isolate (pH 4) | $2.368 \times 10^{-10}$ | $2.33 \times 10^{-11}$ | 6.3 | 29.2 ± 1.8
OWC 9-8-98 Outlet | NA | $3.02 \times 10^{-12}$ | | NR
OWC 9-14-98 RR (pH 4) | $6.32 \times 10^{-10}$ | $9.07 \times 10^{-13}$ | 0.1 | 44.7 ± 5.4
OWC 9-14-98 RR (pH 8) | $3.27 \times 10^{-10}$ | $1.29 \times 10^{-11}$ | 3.9 | 2.97 ± 1.11
5 μM H₂O₂ in MilliQ Water | $1.37 \times 10^{-11}$ | $1.37 \times 10^{-11}$ | 100 | 36.3 ± 4.7

1Measurements reported for this photoreactor system in White (2000) ²$R_{\text{prod}}$ for XAD-8 determined by multiplying the DOC by the production rate determined per mgC/L for this isolate, i.e., 4.00 × 10⁻¹¹ per mgC/L ³The rate of hydroxyl radical production from H₂O₂ is reported to be 2.75 × 10⁻¹² per μM H₂O₂. The production rate was multiplied by the maximum amount of H₂O₂ measured in the samples to determine the amount, at most, of hydroxyl radical that could be formed from H₂O₂ photolysis. ⁴Estimated contribution of H₂O₂ photolysis to total hydroxyl radical production in these samples; reported in % of total ⁵The values for $k_{\text{obs}}$ (corrected for variation in lamp intensity) are reported ± 95% CI ⁶Not reported; value not statistically different from zero.

Table 3.4: Predicted hydroxyl radical production from H₂O₂ in selected water samples and isolates compared to the measured production (White, 2000).
<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>TOC</th>
<th>$\sigma$(M$^\cdot$cm$^{-1}$)</th>
<th>$\Delta$S$_{280-320}$</th>
<th>Nitrates</th>
<th>$F_{\text{Fe}^{2+}}$</th>
<th>$k_{\text{cat}} \times 10^9$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(mg/L)</td>
<td>280nm</td>
<td>320nm</td>
<td>(mM)</td>
<td>(ppb)</td>
<td>(hr$^{-1}$)</td>
</tr>
<tr>
<td>9-14-99 OWC</td>
<td>2.16</td>
<td>9.48 ± 0.04</td>
<td>193</td>
<td>85</td>
<td>0.89</td>
<td>0.0085</td>
<td>5.55 ± 0.14</td>
</tr>
<tr>
<td>RR H$^+$</td>
<td>3.04</td>
<td>9.29 ± 0.07</td>
<td>205</td>
<td>85</td>
<td>0.89</td>
<td>0.0085</td>
<td>2.27 ± 0.32</td>
</tr>
<tr>
<td>Saturated</td>
<td>4.14</td>
<td>9.06 ± 0.04</td>
<td>231</td>
<td>95</td>
<td>0.99</td>
<td>0.0085</td>
<td>1.12 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>5.23</td>
<td>9.18 ± 0.06</td>
<td>221</td>
<td>91</td>
<td>0.90</td>
<td>0.0085</td>
<td>1.33 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>6.75</td>
<td>9.09 ± 0.04</td>
<td>257</td>
<td>119</td>
<td>0.95</td>
<td>0.0085</td>
<td>(ND)$^9$</td>
</tr>
<tr>
<td></td>
<td>7.66</td>
<td>NR$^5$</td>
<td>85</td>
<td>0.95</td>
<td>0.0085</td>
<td>2.74 ± 6.45</td>
<td>11.3 ± 2.3</td>
</tr>
<tr>
<td>Fulton Co. UF</td>
<td>2.12</td>
<td>3.50 ± 0.02</td>
<td>201</td>
<td>93</td>
<td>0.97</td>
<td>0.00304</td>
<td>40.63 ± 0.31</td>
</tr>
<tr>
<td>Isolate$^4$</td>
<td>3.05</td>
<td>3.60 ± 0.01</td>
<td>206</td>
<td>101</td>
<td>0.99</td>
<td>0.00304</td>
<td>37.43 ± 0.87</td>
</tr>
<tr>
<td></td>
<td>4.08</td>
<td>3.49 ± 0.04</td>
<td>250</td>
<td>129</td>
<td>0.97</td>
<td>0.00304</td>
<td>33.70 ± 0.23</td>
</tr>
<tr>
<td></td>
<td>5.11</td>
<td>3.60 ± 0.02</td>
<td>225</td>
<td>114</td>
<td>0.97</td>
<td>0.00304</td>
<td>36.06 ± 0.43</td>
</tr>
<tr>
<td></td>
<td>6.1</td>
<td>3.58 ± 0.01</td>
<td>237</td>
<td>122</td>
<td>0.99</td>
<td>0.00304</td>
<td>35.68 ± 0.68</td>
</tr>
<tr>
<td></td>
<td>7.01</td>
<td>3.73 ± 0.04</td>
<td>220</td>
<td>114</td>
<td>0.96</td>
<td>0.00304</td>
<td>36.99 ± 1.64</td>
</tr>
<tr>
<td></td>
<td>7.96</td>
<td>3.65 ± 0.01</td>
<td>226</td>
<td>116</td>
<td>0.98</td>
<td>0.00304</td>
<td>43.94 ± 1.43</td>
</tr>
<tr>
<td>IHSS Suwanee</td>
<td>2.03</td>
<td>10.08 ± 0.04</td>
<td>350</td>
<td>194</td>
<td>0.85</td>
<td>NA$^7$</td>
<td>10.08 ± 0.24</td>
</tr>
<tr>
<td>River Fulvic</td>
<td>3.08</td>
<td>10.32 ± 0.14</td>
<td>336</td>
<td>187</td>
<td>0.83</td>
<td>NA$^7$</td>
<td>1.16 ± 0.28</td>
</tr>
<tr>
<td>Acid$^4$</td>
<td>4.13</td>
<td>10.28 ± 0.06</td>
<td>353</td>
<td>196</td>
<td>0.83</td>
<td>NA$^7$</td>
<td>1.19 ± 0.61</td>
</tr>
<tr>
<td></td>
<td>5.04</td>
<td>10.46 ± 0.01</td>
<td>352</td>
<td>197</td>
<td>0.83</td>
<td>NA$^7$</td>
<td>0.57 ± 0.34</td>
</tr>
<tr>
<td></td>
<td>6.04</td>
<td>10.30 ± 0.06</td>
<td>361</td>
<td>205</td>
<td>0.82</td>
<td>NA$^7$</td>
<td>0.76 ± 0.65</td>
</tr>
<tr>
<td></td>
<td>7.02</td>
<td>10.09 ± 0.07</td>
<td>371</td>
<td>213</td>
<td>0.83</td>
<td>NA$^7$</td>
<td>1.77 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>8.02</td>
<td>10.18 ± 0.13</td>
<td>370</td>
<td>216</td>
<td>0.82</td>
<td>NA$^7$</td>
<td>5.11 ± 4.41</td>
</tr>
</tbody>
</table>

1 Measured pH of experimental solution  
2 Phosphate buffer (5mM)  
3 Where ± values are one standard deviation for replicate samples  
4 NR: not reported: values not statistically different from zero  
5 Molar absorptivity (normalized for carbon and corrected for nitrate absorption) at $\lambda = 280$ and 320 nm  
6 Light screening factor calculated for $\lambda$'s 290-375 nm  
7 NA not applicable  
8 ND not detected  
9 The values for $k_{\text{cat}}$ (corrected for variation in lamp intensity) are reported ± 95% CI.

Table 3.5: Effect of pH on the rate coefficient of alachlor transformation in selected NOM isolates and proton saturated OWC 9-14-99 RR.

195
<table>
<thead>
<tr>
<th>Sample</th>
<th>pH $^1$</th>
<th>TOC $^2$</th>
<th>$e^2(M^{-1}cm^{-1})$</th>
<th>$\Sigma_{290-375}$</th>
<th>% Aromaticity$^4$</th>
<th>% Aliphaticity$^4$</th>
<th>% Carboxylic Acid$^4$</th>
<th>% Carboxyl$^4$</th>
<th>Fe$_{Total}^3$ (ug/L)</th>
<th>$k_{obs} \times 10^3$ (hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRFA</td>
<td>3.61</td>
<td>7.94 ± 0.04</td>
<td>343</td>
<td>196</td>
<td>0.86</td>
<td>31.4</td>
<td>68.6</td>
<td>21.3</td>
<td>5.6</td>
<td>2.94 ± 0.17</td>
</tr>
<tr>
<td>LFFA</td>
<td>3.60</td>
<td>8.15 ± 0.05</td>
<td>157</td>
<td>69</td>
<td>0.94</td>
<td>15.8</td>
<td>84.2</td>
<td>19.0</td>
<td>7.8</td>
<td>6.26 ± 0.21</td>
</tr>
<tr>
<td>OWC XAD-8</td>
<td>4.08</td>
<td>9.20 ± 0.01</td>
<td>326</td>
<td>166</td>
<td>0.85</td>
<td>22.0</td>
<td>78.0</td>
<td>17.9</td>
<td>3.4</td>
<td>0.82 ± 0.43</td>
</tr>
<tr>
<td>Fulton Co. UF</td>
<td>4.08</td>
<td>3.49 ± 0.04</td>
<td>250</td>
<td>129</td>
<td>0.97</td>
<td>13.0</td>
<td>87.0</td>
<td>14.7</td>
<td>1.1</td>
<td>33.70 ± 0.23</td>
</tr>
</tbody>
</table>

$^1$ Phosphate buffer (5mM) $^2$ Measured pH of experimental solution $^3$ Where ± values are one standard deviation for replicate samples $^4$ The $^{13}$C NMR data taken from literature (McKnight et al., 1994; Ravichandran et al., 1998; McKnight et al., 1991; White, 2000) $^5$ Molar absorptivity (normalized for carbon and corrected for nitrate absorption) at $\lambda = 280$ and 320 nm $^6$ Light screening factor calculated for $\lambda$'s 290-375 nm $^7$ The values for $k_{obs}$ (corrected for variation in lamp intensity) are reported ± 95% CI.

Table 3.6: Reported properties for NOM isolate samples used in this study.
<table>
<thead>
<tr>
<th>Sample</th>
<th>pH$^1$</th>
<th>TOC$^2$ (mgC/L)</th>
<th>$\Sigma S_{290-375}$</th>
<th>$\text{Fe}_{\text{Total}}^{\text{added}}$ (ppb)</th>
<th>$\text{Fe}_{\text{Total}}^{\text{measured}}$ (ppb)</th>
<th>$k_{\text{obs}}^{\text{7} \times 10^3}$ (hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Buffered MilliQ</strong>$^2$</td>
<td>8.08</td>
<td>NR$^3$</td>
<td>1</td>
<td>--</td>
<td>ND$^6$</td>
<td>1.53 ± 0.28</td>
</tr>
<tr>
<td></td>
<td>4.21</td>
<td>NR$^5$</td>
<td>1</td>
<td>--</td>
<td>0.53 ± 13.42</td>
<td>NR$^8$</td>
</tr>
<tr>
<td><strong>Fe Blank</strong></td>
<td>8.14</td>
<td>0.12 ± 0.05</td>
<td>1</td>
<td>116</td>
<td>129.09 ± 0.53</td>
<td>5.84 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>4.03</td>
<td>0.02 ± 0.01</td>
<td>1</td>
<td>117</td>
<td>90.92 ± 0.94</td>
<td>32.5 ± 4.3</td>
</tr>
<tr>
<td><strong>SRFA Blank</strong></td>
<td>8.02</td>
<td>10.18 ± 0.13</td>
<td>0.82</td>
<td>--</td>
<td>5.11 ± 4.41</td>
<td>16.7 ± 5.6</td>
</tr>
<tr>
<td></td>
<td>4.02</td>
<td>9.88 ± 0.06</td>
<td>0.86</td>
<td>--</td>
<td>1.81 ± 0.19</td>
<td>22.4 ± 1.3</td>
</tr>
<tr>
<td><strong>SRFA with Fe Amendment</strong></td>
<td>8.19</td>
<td>10.30 ± 0.09</td>
<td>0.82</td>
<td>116</td>
<td>125.03 ± 5.29</td>
<td>16.6 ± 2.5</td>
</tr>
<tr>
<td></td>
<td>4.03</td>
<td>9.70 ± 0.05</td>
<td>0.86</td>
<td>118</td>
<td>181.26 ± 0.91</td>
<td>102.6 ± 10.3</td>
</tr>
<tr>
<td><strong>OWC 9-14-99 RR</strong></td>
<td>8.00</td>
<td>11.03 ± 0.03</td>
<td>0.92</td>
<td>--</td>
<td>10.00 ± 3.66</td>
<td>2.97 ± 1.11</td>
</tr>
<tr>
<td></td>
<td>4.08</td>
<td>11.33 ± 0.15</td>
<td>0.92</td>
<td>--</td>
<td>12.53 ± 0.59</td>
<td>44.7 ± 5.4</td>
</tr>
<tr>
<td><strong>OWC 9-14-99 RR H$^+$ Sat.</strong></td>
<td>7.66</td>
<td>NR$^4$</td>
<td>0.95</td>
<td>--</td>
<td>2.74 ± 6.45</td>
<td>11.3 ± 2.3</td>
</tr>
<tr>
<td></td>
<td>4.14</td>
<td>9.06 ± 0.04</td>
<td>0.99</td>
<td>--</td>
<td>1.12 ± 0.12</td>
<td>27.4 ± 4.6</td>
</tr>
<tr>
<td><strong>OWC 9-14-99 RR H$^+$ Sat. with Fe</strong></td>
<td>4.10</td>
<td>9.56 ± 0.06</td>
<td>0.99</td>
<td>120</td>
<td>145.9 ± 0.28</td>
<td>177 ± 18</td>
</tr>
</tbody>
</table>

$^1$ Measured pH of experimental solution  
$^2$ Phosphate buffer (5mM)  
$^3$ Where ± values are one standard deviation for replicate samples  
$^4$ NR: not reported; values not statistically different from zero  
$^5$ Light screening factor calculated for λ's 290-375 nm  
$^6$ ND not detected  
$^7$ The values for $k_{\text{obs}}$ (corrected for variation in lamp intensity) are reported ± 95% CI  
$^8$ NR: not reported; the measured $k_{\text{obs}}$ was statistically zero.

Table 3.7: Effect of iron amendments on alachlor degradation in SRFA and OWC 9-14-99 RR water.
<table>
<thead>
<tr>
<th>Sample</th>
<th>pH (measured)</th>
<th>Fe&lt;sub&gt;total&lt;/sub&gt; (ppb)</th>
<th>Fe&lt;sup&gt;3+&lt;/sup&gt;</th>
<th>Fe(OH)&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Fe(OH)&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</th>
<th>FeOH&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>FeHPO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</th>
<th>FeH&lt;sub&gt;2&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>FeSO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buffered MilliQ</td>
<td>8.08</td>
<td>4.21 0.53 ± 13.42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe Blank</td>
<td>8.14</td>
<td>4.03 90.92 ± 0.94</td>
<td>&lt; 0.01</td>
<td>76</td>
<td>22</td>
<td>2</td>
<td>57</td>
<td>8</td>
<td>35</td>
</tr>
<tr>
<td>SRFA Blank</td>
<td>8.02</td>
<td>4.02 1.81 ± 0.19</td>
<td>&lt; 0.01</td>
<td>84</td>
<td>9</td>
<td>7</td>
<td>51</td>
<td>8</td>
<td>41</td>
</tr>
<tr>
<td>SRFA with Fe Amendment</td>
<td>8.19</td>
<td>4.03 181.26 ± 0.91</td>
<td>&lt; 0.01</td>
<td>76</td>
<td>22</td>
<td>2</td>
<td>57</td>
<td>8</td>
<td>35</td>
</tr>
<tr>
<td>OWC 9-14-99 RR</td>
<td>8.00</td>
<td>4.08 12.53 ± 0.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>OWC 9-14-99</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9-14-99 OWC RR H&lt;sup&gt;+&lt;/sup&gt; Sat.</td>
<td>7.66</td>
<td>4.14 1.12 ± 0.12</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>88</td>
<td>11</td>
<td>&lt;1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9-14-99 OWC RR H&lt;sup&gt;+&lt;/sup&gt; Sat. with Fe</td>
<td>4.10</td>
<td>145.9 ± 0.28</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>89</td>
<td>11</td>
<td>&lt;1</td>
<td></td>
<td></td>
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</tbody>
</table>

<sup>1</sup> Calculations showed that concentrations of iron as Fe<sup>3+</sup>, FeCl<sup>2+</sup>, Fe<sub>2</sub>(OH)<sub>2</sub><sup>+</sup>, FeCl<sub>2</sub><sup>+</sup>, Fe<sub>3</sub>(OH)<sub>4</sub><sup>+</sup>, FeCl<sub>3</sub> would be negligible. These calculations ignore the iron-NOM species. 
<sup>2</sup> Solutions were buffered with 5 mM phosphate buffer. 
<sup>3</sup> Below detection limit 
<sup>4</sup> Not applicable

Table 3.8: Iron speciation (calculated as % of total) in water samples used for the iron amendment experiments. Binding of iron by NOM was not considered.
### Table 3.9: Effect of iron level on the photoinduced degradation of alachlor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe Added (ppb)</th>
<th>pH</th>
<th>TOC (mg/L)</th>
<th>$a(M^{-1}cm^{-1})$</th>
<th>$\Sigma_{280-375}$</th>
<th>FeTotal (ppb)</th>
<th>$k_{obs} \times 10^3$ (hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe Control</td>
<td>0</td>
<td>3.66</td>
<td>0.17 ± 0.04</td>
<td>2.94 ± 0.17</td>
<td>1.86 ± 1.03</td>
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<tr>
<td></td>
<td>2</td>
<td>3.61</td>
<td>NA</td>
<td>6.26 ± 0.21</td>
<td>5.54 ± 0.48</td>
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<tr>
<td></td>
<td>5</td>
<td>3.62</td>
<td>NA</td>
<td>9.15 ± 0.39</td>
<td>8.89 ± 0.81</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.62</td>
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<td>13.36 ± 0.42</td>
<td>12.1 ± 1.09</td>
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<td></td>
</tr>
<tr>
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<td>20</td>
<td>3.59</td>
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<td>22.99 ± 1.05</td>
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<tr>
<td></td>
<td>30</td>
<td>3.63</td>
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<td>27.68 ± 0.20</td>
<td>35.4 ± 2.04</td>
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<td>40</td>
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<td>32.1 ± 0.22</td>
<td>39.7 ± 2.24</td>
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<tr>
<td></td>
<td>50</td>
<td>3.61</td>
<td>NA</td>
<td>36.22 ± 0.41</td>
<td>48.2 ± 2.05</td>
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<td>SRFA</td>
<td>0</td>
<td>3.61</td>
<td>7.94 ± 0.04</td>
<td>343</td>
<td>190</td>
<td>0.86</td>
<td>1.82 ± 0.15</td>
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<td>3.59</td>
<td>7.93 ± 0.01</td>
<td>4.02 ± 0.39</td>
<td>14.4 ± 0.99</td>
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<td>5</td>
<td>3.60</td>
<td>8.00 ± 0.08</td>
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<td>7.98 ± 0.05</td>
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<td>26.5 ± 2.43</td>
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<td>8.07 ± 0.07</td>
<td>23.0 ± 0.11</td>
<td>34.1 ± 1.45</td>
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<td>8.15 ± 0.04</td>
<td>33.07 ± 0.40</td>
<td>41.7 ± 1.65</td>
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<tr>
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<td>40</td>
<td>3.60</td>
<td>8.20 ± 0.25</td>
<td>43.23 ± 0.20</td>
<td>45.6 ± 3.15</td>
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<td>8.16 ± 0.08</td>
<td>53.37 ± 0.69</td>
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<td>LFFA</td>
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<td>8.15 ± 0.05</td>
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<td>0.94</td>
<td>2.71 ± 0.08</td>
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<td>3.60</td>
<td>8.06 ± 0.04</td>
<td>4.49 ± 0.40</td>
<td>15.0 ± 0.82</td>
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</tr>
<tr>
<td></td>
<td>5</td>
<td>3.59</td>
<td>7.98 ± 0.03</td>
<td>7.33 ± 0.23</td>
<td>19.0 ± 1.19</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.59</td>
<td>8.20 ± 0.02</td>
<td>12.81 ± 0.07</td>
<td>21.4 ± 1.38</td>
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<tr>
<td></td>
<td>20</td>
<td>3.60</td>
<td>8.20 ± 0.03</td>
<td>23.59 ± 0.01</td>
<td>26.3 ± 1.60</td>
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<tr>
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<td>30</td>
<td>3.60</td>
<td>8.02 ± 0.06</td>
<td>34.01 ± 0.41</td>
<td>30.7 ± 1.24</td>
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</tr>
<tr>
<td></td>
<td>40</td>
<td>3.58</td>
<td>8.09 ± 0.07</td>
<td>43.81 ± 0.34</td>
<td>33.2 ± 1.62</td>
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</tr>
<tr>
<td></td>
<td>50</td>
<td>3.60</td>
<td>8.18 ± 0.05</td>
<td>55.00 ± 0.64</td>
<td>36.1 ± 1.67</td>
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</tbody>
</table>
8-ethyl-1-methoxy-methyl-4-methyl-2-oxo-1,2,3,4-tetraquinoline

Figure 3.1: Proposed scheme for the direct photolysis of alachlor (adapted from Schmidt, et al., 1995 and Penuela and Barcelo, 1996).
Figure 3.2: Map of Old Woman Creek Estuarine Reserve (OWC), Huron, OH. Water samples were obtained from the Inlet (IN), Railroad (RR), and Outlet (OUT).

Figure 3.3: Peroxidase-catalyzed oxidation of Leuco Malachite Green by hydrogen peroxide (Zepp et al., 1988).
Figure 3.4: Comparison of the measured photoinduced degradation of alachlor in Old Woman Creek water samples at the natural pH (~8) and pH adjusted samples.
Figure 3.5: Comparison of the photoinduced degradation of alachlor in various engineered wetlands located in agricultural watersheds. Data from two pHs are presented. Error bars represent the 95% CI determined from least squares analysis of the data.
Figure 3.6: Molar absorptivities (M$^{-1}$cm$^{-1}$) of modified samples of the OWC 9-14-99 RR raw water.

Figure 3.7: Observed pseudo-first order rate coefficient determined from experiments conducted with modified samples of the OWC 9-14-99 RR wetland water sample.
Figure 3.8: Correlation between the DOC level measured in the wetland water samples and the factor that alachlor degradation was promoted at the lower pH. The Champaign Co. water was not included in this plot.
Figure 3.9: Correlations of $k_{\text{obs}}$ (hr$^{-1}$) and the TOC level in wetland water samples at high (a) and low (b) pH. Error bars represent the 95% CI of determined rate coefficients. Note that the data from the OWC 6-29-98 IN samples were not included on these plots. Outliers in plot (a) were the Fulton Co. and the OWC 9-14-99 RR waters.
Figure 3.10: Plots of $k_{obs}$ (hr$^{-1}$) versus the molar absorptivity at 320 nm and 280 nm at the high (a) and low (b) pH wetland water samples. MilliQ water controls are also included in the plots. The rate constant for the OWC 6-29-98 IN water was corrected for the nitrate contribution (0.0978 hr$^{-1}$).
Figure 3.11: Timecourses presented comparing the photodegradation of alachlor in OWC XAD-8 isolate at high and low pH to natural waters of similar composition.
Figure 3.12: Plot of total iron (Fe_{Total}) measured in the wetland water samples versus the factor that the reactions were promoted upon lowering the pH of the samples.

Figure 3.13: Correlation between Fe(ppb):TOC (mgC/L) ratio to observed rate coefficient for alachlor degradation.
Figure 3.14: Relationship of OWC XAD-8 TOC (mgC/L) to $k_{\text{obs}}$ (hr$^{-1}$) for alachlor photodegradation. Data presented are for the uncorrected (black) and corrected (white) for inner filter effects values of $k_{\text{obs}}$. Line indicates model fit.

Figure 3.15: Correlation between TOC and $k_{\text{obs}}$ (normalized to the TOC and corrected for light screening effects) for alachlor degradation promoted by the OWC XAD-8.
Figure 3.16: The levels of H$_2$O$_2$ measured in several of the OWC water samples during timecourses.
Figure 3.17: Rate coefficients measured for alachlor degradation ($k_{\text{obs}}$) (left axis) and iron levels measured (right axis) plotted against the pH for selected NOM isolates and the proton saturated OWC 9-14-99 RR wetland water sample.
Figure 3.18: Plot of normalized (to the TOC) rate coefficient measured for alachlor degradation versus the pH for selected NOM isolates and proton saturated OWC 9-14-99 RR wetland water sample.
Figure 3.19: Plot of the normalized (to the TOC and Fe) rate coefficient measured for alachlor degradation versus the pH. Error bars are the calculated propagated error for the normalization calculation based upon the standard deviations of all measured values.
Figure 3.20: The effect that addition ~2 μM Fe to SRFA solutions had on $k_{obs}$ for the photoinduced degradation of alachlor.
Figure 3.21: The effect that addition of ~2 μM Fe to OWC 9-14-99 RR water samples had on the normalized (to [TOC]) $k_{obs}$ for the photoinduced degradation of alachlor.

Figure 3.22: Photoinduced degradation of alachlor in SRFA and LFFA solutions. Results are compared with those obtained from irradiation of alachlor in buffered MilliQ water and NOM solutions that had been spiked with either or both methanol (0.05 M; MeOH; light gray bars) and iron (~25 ppb Fe; black bars).
Figure 3.23: Effect of Fe_{Total} (ppb) on the measured rate coefficient for the photoinduced degradation of alachlor in selected NOM isolate solutions (pH = 3.60).
Figure 3.24: Molar absorptivities ($M^{-1}cm^{-1}$) calculated for the SRFA and LFFA solutions as a function of wavelength. For comparison, the molar absorptivity of the Suwannee River raw water is also shown.
Figure 3.25: Extrapolation of $k_{obs}$ for alachlor degradation from linear portion of NOM vs $Fe_{Total}$ plots. (a) SRFA and (b) LFFA
Figure 3.26: Comparison of $k_{\text{pred}}$ and $k_{\text{obs}}$ for the iron promoted degradation of alachlor in reconstituted SRFA (a) and LFFA (b).
CHAPTER 4

THE REACTIVITY OF NATURAL WATERS TOWARD CONTAMINANT DEGRADATION: PHOTOCHEMICAL BEHAVIOR OF NATURAL ORGANIC MATTER

4.1 Introduction

The research reported thus far has examined the photoinduced degradation of some prevalent agricultural contaminants, carbaryl and alachlor. While carbaryl was susceptible to photochemical reactions at all pHs measured, alachlor was not. In both cases, the data provided evidence that the reactions were mediated by the NOM and corroborates several other studies (Canonica et al., 1995; Canonica and Freiburghaus, 2001; Chiron et al., 1995; Hoigné, 1990; Minero, et al., 1992; Kolpin and Kalkhoff, 1993; Faust and Zepp, 1993; Frimmel and Hessler, 1994; Simmons and Zepp, 1986; Fukushima and Tatsumi, 2001). In order to understand how NOM mediates these reactions, the photochemical behavior of the NOM must be examined.

Dissolved natural organic matter is the most important attenuator of light in natural waters (Davies-Colley and Vant, 1987; Scully and Lean, 1994; Markager and Vincent, 2000; Gao and Zepp, 1998). Hence, the photoreactive fraction of dissolved natural organic matter is referred to as chromophoric dissolved organic matter (CDOM).
As has been examined (Section 1.3), CDOM readily generates a host of reactive intermediates and free radicals (HO*, H₂O₂, O₂−, ¹O₂, R*, ROO* and ²NOM) upon absorption of sunlight, especially in the UVB and UVA regions (Figure 1.1) (Zepp et al., 1985; Faust et al., 1987; Cooper et al., 1989; Hoigné et al., 1990; Haag et al., 1990; Bruccoleri et al., 1993; Miller, 1994; Canonica et al., 1995; Blough and Zepp, 1995; Sandvik et al., 2000). Because many pollutants do not strongly absorb sunlight, the reaction of contaminants with these reactive intermediates may be a more important degradative pathway than direct photolysis. Thus, any process that alters the chemical nature of the NOM may affect its ability to mediate the degradation of contaminants.

4.1.1 Photobleaching

Direct and indirect photolysis modify NOM’s chemical structure. Early research on this phenomenon observed that colored humic substance solutions became “paler” in color upon exposure to irradiation (Bricaud et al., 1981; Davies-Colley and Vant, 1987). This fading is referred to as photobleaching (Moran and Zepp, 1997). Photobleaching now refers to any change in the light absorbing properties of the CDOM induced by photochemical reactions. Observed changes include a decrease in the ability of NOM to absorb light and a shift in the relative proportions of chromophores absorbing in specific-wavelength regions (Sandvik et al., 2000; Gao and Zepp, 1998). The structural changes that manifest themselves in these photochemical property changes include the fragmentation of NOM into smaller macromolecules having smaller, average molecular
weights (Kieber et al., 1990; Bertilsson and Tranvik, 2000; Gao and Zepp, 1998; Moran and Zepp, 1997; Miller and Moran, 1997; Opashl and Benner, 1998; Whitehead et al., 2000). As a result of the fragmentation, the relative ratios of elements will change. For example, the oxygen to carbon (O/C) ratio increases during photolysis of CDOM as oxygen is incorporated into the NOM matrix (NOM becoming more oxidized) (Schmitt-Kopplin et al., 1998; Andrews et al., 2000). Moreover, the nitrogen and carbon ratio may also decrease as bound nitrogen can be photochemically released as nitrite (Kieber et al., 1999) and ammonium (Bushaw et al., 1996).

In addition, reactive non-NOM water constituents may also transform NOM through indirect processes, which, in turn, could influence NOM photochemistry. When irradiated with sunlight, nitrate and nitrite are capable of producing hydroxyl radicals (HO•) with quantum yields ranging from 9.2 − 17 × 10⁻³ (Mabury and Crosby, 1994) and 0.015 to 0.08 (Zafiriou and Bonneau, 1987), respectively. Furthermore, superoxide can react with hydronium ions to form H₂O₂. In the presence of trace metals (Fe(II), Cu(I)), H₂O₂ can produce HO• through the Fenton reaction (Cooper et al., 1983; Faust et al., 1993). Depending on the water quality parameters, such processes may produce steady-state concentrations of HO• sufficient to oxidize NOM through secondary reactions.

There are two common methods of monitoring photobleaching. The first is to measure the loss of sample absorbance as a function of irradiation time using UV/VIS spectrophotometry (Kieber et al., 1990; Whitehead et al., 2000). For dilute solutions, the absorbance will decay exponentially and can be modeled according to first-order degradation kinetics (Gao and Zepp, 1998). For optically dense solutions, this decay
follows zero order kinetics (Zepp and Cline, 1977; Whitehead et al., 2000). Analyzing the absorbance decay kinetics yields a pseudo-first order rate coefficient for photobleaching. This parameter, however, can be deceptive because while chromophores that absorb in one UV/VIS region may be photobleached, chemical transformation of the CDOM may result in the formation of new chromophores that absorb in other wavelength regions, and the measured absorbance that corresponds to that region will increase. For example, as CDOM becomes more oxidized, there will be an increase in the absorbance in the UVB region (\(\lambda = 280 - 320\) nm) where carbonyl groups absorb light. The end result of the decay and growth of chromophores in the CDOM matrix shifts the shape of the absorbance curve.

The second method of monitoring photobleaching is to examine the changes that photobleaching causes in the spectral characteristics of the UV/VIS absorbance curve of CDOM. Changes in the absorbance curve suggest that a shift has occurred in the CDOM chromophores. In general, the UV/VIS absorption spectrum for CDOM solution is a featureless curve that exponentially decreases with an increase in wavelength (for the wavelength region that overlaps with the solar spectrum) and has no distinct bands (Figure 3.24 for examples SRFA/LFFA spectra) (Miller, 1994). The decrease of this curve fits an exponential model very well (Bricaud et al., 1981; Zepp and Schlotzhauer, 1981; Davies-Colley and Vant, 1987; Green and Blough, 1994; Sanvik et al., 2000). In this model, the decrease in absorbance is related to the wavelength by:
\[ \alpha_\lambda = Ae^{S(k_{\lambda, 400-\lambda})} \]  

Where A is a constant, "S" (which is the slope from the linear regression of the log-transformed data) is the coefficient governing the "rate" of decay with respect to the wavelength \((d\alpha_\lambda/d_\lambda)\) and "\(\alpha_\lambda\)" is the absorption coefficient \((m^{-1})\) specific to wavelength \(\lambda\).

Thus, "S" quantifies the ratio of the longer wavelength absorbers (UVA \((i.e., \lambda = 320-400 \text{ nm})\) and visible regions) to shorter wavelength absorbers (UVB). Shorter wavelength absorbers have been affiliated not only with aromatic species (Traina et al., 1990; Chin et al., 1994) but also with low molecular weight (LMW) organic compounds (Miller, 1994; Gao and Zepp, 1998; Whitehead et al., 2000). There is some evidence in the literature that LMW compounds contribute positively to UVB absorbance and therefore, to the value of "S". Miller (1994) noted that CDOM of incubated estuarine samples having the lowest mean molecular weights had the highest measured "S" values. Furthermore, Sandvik et al. (2000) attributed the decrease in measured "S" values for a retentate compared to raw water isolated by ultrafiltration to the loss of LMW species through the membrane. Finally, Mopper et al. (1996) measured "S" values from various fractions of a coastal water isolated by ultrafiltration. They attributed the decrease in "S" for the retentate and the increase in "S" for the permeate to the concentration of longer wavelength absorbers (which corresponds to higher molecular weight material) in the retentate and the concentration of shorter wavelength absorbers (the LMW species that had passed through the membrane) in the permeate.
Likewise, in some experiments, photobleaching caused “S” to decrease for a number of CDOM isolates and natural water samples (Miller, 1994; Gao and Zepp, 1998). Alternatively, “S” has also been found to increase in estuary water isolated in mesocosms after irradiation and was attributed to: (1) the slower photobleaching of low molecular weight (LMW) CDOM relative to higher molecular weight (HMW) CDOM as reported in Gao and Zepp (1998); (2) the high optical density of mesocosm solutions in which zero-order kinetics would dictate that photobleaching and chromophores with smaller initial absorbances would have a smaller half-life; or (3) the biological expulsion of LMW substances in situ to increase the LMW chromophore pool (Whitehead et al., 2000). On the basis of the literature, it stands to reason that any process that would contribute to the LMW pool should cause “S” to increase. Thus, an “S” factor that increases with irradiation time indicates that the ratio of shorter wavelength absorbers to longer wavelength absorbers is increasing and may be interpreted to indicate that photobleaching of CDOM shifts the structural character of the NOM to lower molecular weight species such as carbonyls or carboxylic acids.

4.1.2 Application of Photobleaching Data to the Study of Photochemical Processes Occurring in Natural Waters

Since the changes in both the measured absorbance loss and spectral characteristics are proportional to absorption of light by CDOM, any secondary process arising from photolysis of CDOM should also be proportional to these properties (Gao
and Zepp, 1998; Sandvik, 2000). Indeed, photobleaching measurements have been used to quantify changes in the chromophoric nature of NOM and were correlated to a number of secondary processes that occurred as a result of NOM photochemistry. Photobleaching rates were related to absorbed radiation (Whitehead et al., 2000; Bertilsson and Tranvik, 2000), Chlorophyll a levels (i.e., rate of biological growth) (Whitehead et al., 2000; Davies-Colley and Vant, 1987), biomass production and bacterial activity (Moran and Zepp, 1997; Miller and Moran, 1997; Benner and Biddanda, 1998), O₂ consumption (Andrews et al., 2000), ROS production (Scully et al., 1997; Andrews et al., 2000; Sandvik et al., 2000), dissolved inorganic carbon (DIC) production (Miller and Zepp, 1995; Gao and Zepp, 1998), production of carbon monoxide (Valentine and Zepp, 1993; Zuo and Jones, 1997; Gao and Zepp, 1998), production of LMW compounds (i.e., organic aldehydes, ketones, and acids) (Kieber et al., 1990), and mineralization of CDOM (Vähätalo et al., 2000). Thus, based upon the literature, if contaminants are reacting with ROS or reactive intermediates generated directly from photolysis of CDOM, then the degradation rates of contaminants should be related to photobleaching data as well.

4.1.3 Goals of the this Study

Bertilsson and Tranvik (2000) comment that the presence of certain water constituents (H⁺ as indicated by pH dependency), iron, inorganic ions (conductivity) influenced the variability of DIC produced in their experiments. This study points to the importance of considering the influence that other non-NOM natural water constituents
will have on these reactions. The current study will systematically investigate how non-
NOM constituents affect the photobleaching of the NOM. Specifically, I investigated the
photobleaching of the CDOM in a number of natural water and NOM isolates. I studied
the change in "S" factors and measured absorbance degradation coefficients under
varying sample solution conditions. I considered the influence of oxygen, hydroxyl
radical quenchers, pH, TOC, NOM source, and Fe levels on the photobleaching
parameters. Finally, I determined the relationship between these results and the alachlor
degradation observed to occur in these samples to evaluate whether or not the
photobleaching could be correlated to contaminant degradation. In this way, I hope to
ascertain the level of involvement that NOM has in promoting contaminant degradation.

4.2 Methods

4.2.1 Materials

All chemicals and reagents were purchased commercially and used without further
purification. Chemicals and reagents were acquired from the following: Alachlor
(99.5%) from Chem Services West Chester, PA; potassium phosphate monobasic from
(KH$_2$PO$_4$; Certified ACS reagent ), sulfuric acid (Reagent Grade), sodium bisulfite (ACS
Reagent), methanol (Optima), acetonitrile (Optima), hexane (Optima), sodium hydroxide
solution (50 % w/w), and glacial acetic acid (Certified ACS plus) from Fisher Scientific;
potassium phosphate, dibasic powder (K$_2$HPO$_4$), sodium phosphate, dibasic Na$_2$HPO$_4$·12H$_2$O (12-hydrate), sodium phosphate, monobasic monohydrate NaH$_2$PO$_4$·H$_2$O, from J.T. Baker, INC. (Phillipsburg, N.J.); hydrogen peroxide (30%), sodium hydroxide (NaOH; analytical reagent) from Mallinckrodt; potassium hydrogen phthalate (KHP), ferric chloride, sodium borate, p-nitroanisole, and pyridine from Aldrich (Milwaukee, WI); Argon (4.8 grade) from Praxair. Suwannee River fulvic acid, Lake Fryxell fulvic acid from G. Aiken (USGS, Boulder, CO). Purified water (18 Ω) was produced from a Milli-Q water system (Millipore Corp., Bedford, MA). All glassware and plastic were acid washed either with NOCHROMIX Cleaning Reagent (Godax Laboratories, Inc) in concentrated sulfuric acid or 10% HCL prior to use.

4.2.2 Water Samples and NOM Isolates

The wetland water samples and NOM isolates used for these studies were obtained from the field sites or commercially and characterized as previously described in Section 3.2.2.1. All samples were analyzed for UV/VIS absorbance, TOC, pH, inorganic anions, alkalinity, and Fe content as described in Section 3.2.2.2.

4.2.3 Photolytic Reactions.

The photochemical reactor and procedure used for photochemical reactions is described elsewhere (Section 2.2 and 3.2.3). The average temperature of the reactor over
the course of these experiments was $42 \pm 3 \, ^\circ C$ in the photoreactor. Samples were sacrificed periodically in order to monitor changes in CDOM as a function of irradiation time.

4.2.4 Actinometry and Light Intensity Corrections

Actinometric corrections were performed as described in Section 3.2.4 when necessary (i.e., when data was compared where lamp intensity changed significantly).

4.2.5 Photobleaching Data Analysis

CDOM transformation was monitored using a dual-beam UV/VIS spectrophotometer (Cary 1, Varian). Samples were scanned from 200 to 700 nm in quartz cuvettes having a 1 cm (0.01 m) pathlength. The absorbance from the UV-VIS data was transformed into an absorption coefficient, $\alpha_\lambda (m^{-1})$, at a specific wavelength $\lambda$ by:

$$\alpha_\lambda = \frac{2.303 \times \text{ABS}}{l} \quad (4.2)$$

where $l$ is the pathlength (in meters). The limit of detection (to distinguish a signal from baseline noise) was determined in the region of 600-700 nm where the contribution to sample absorbance from dissolved water constituents would be minimal. The detection limit was 0.0006 ABS units (on Cary 1). Following, the acceptable level for the determination of the absorption coefficient, $\alpha(\lambda)$ would be 0.139. For the data fitting, data was eliminated from the fits that did not meet this criterion. The value of "$S$" was
determined according to published methods (Green and Blough, 1994). Absorption coefficients from a scan were then “fitted” using least squares analysis to the following exponential decay function to determine the “S” factor:

\[
\alpha_{\lambda} = \alpha_{\lambda,r} e^{S(r-\lambda)}
\]  

(4.3)

where \(\alpha_{\lambda,r}\) is the absorption coefficient at a reference wavelength, \(\lambda_r\) (Bricaud et al., 1981; 1981; Davies-Colley and Vant, 1987; Sandvik et al., 2000; Green and Blough, 1994). The reference wavelength is used to normalize for differences between samples.

Since the values of “S” are dependent on the wavelength range chosen for study (Sandvik et al., 2000), I selected the region from 290-450 nm to determine the “S” factor. The lower limit was chosen at 290 nm since this is the cut-off wavelength for overlap with the solar spectrum and also, where alachlor absorption does not influence the absorption spectra of the samples (since these UV-VIS were taken of the reaction mixtures). The upper limit was chosen at 450 nm because above this wavelength, the water constituents in these samples absorbed minimally, i.e., close to the limit of detection.

Samples were not corrected for backscattering (Bricaud et al., 1981) or refractive index differences (Green and Blough, 1994). The literature reveals a difference in opinion as to the cause of deviations of \(\alpha_{\lambda}\) absorption spectra for various marine waters (Green and Blough, 1994). For these samples, the back scattering (or refractive index correction) was found to be negligible in the regions that it would be observed (> 600 nm). A high backscattering or refractive index correction would not be expected for these
fresh water samples due to their low ionic strength relative to seawater samples (Green and Blough, 1994).

Because of the enormous data sets (over 700 scans) a computer program was written (C++) that would analyze the data from sets. An algorithm was written to transform the absorbance data 290-450 nm into absorption coefficients (Equation 4.2) and determine the magnitude of "S" yielding the "best fit" to the absorption coefficient curve (Equation 4.3) via gradient descent. A non-linear optimization was used to minimize the sum of the squares of error. Because the solutions more closely approximated a dilute solution model than an optically dense solution, a pseudo-first order model was used to determine the rate coefficients for the absorption coefficient degradation as a function of time for a given wavelength. The program first took the natural logarithms of the absorption coefficients and calculated the "best fit" to the linear model using least squares analysis. The slope of the line yields the value of the pseudo-first order degradation coefficient.

The data generated from the program were validated by comparing the results with those obtained by the analysis of individual scans using the software packages Excel (Microsoft) and Sigma Plot 2000 (v.6, SPSS inc.) Not only did the computer program return values that were, in most cases, the same to the number of significant digits as the individual data manipulation, but also the minimization of error achieved by the computer program was consistently lower for the validation samples than what could be achieved by individual data analysis (Figure 4.1). Hence, I felt confident in applying this program to the entire data set.

232
4.3 Results and Discussion

The following sections report and discuss the results from several sets of experiments that tested the effects on observed photobleaching from:

1) varying solution conditions in the most reactive, low nitrate containing natural water (OWC 9-14-99 RR sample); (2) varying the level of TOC; (3) changing the pH of reaction solutions; and (4) the presence of trace metals (Fe).

4.3.1 Photobleaching studies with the Old Woman Creek Water

The effect that certain water constituents have on photobleaching was studied in the OWC 9-14-99 RR sample. Alachlor was observed to degrade very efficiently in this low nitrate containing water sample in a photochemical process presumed to be promoted by the NOM (Section 3.3.4). The photobleaching of the OWC 9-14-99 RR sample was studied in a number of solutions that had been altered in several ways including: (1) adjusting the pH from 8.00 to 4.08; (2) sparging with argon; (3) adding methanol as a HO· scavenger; and (4) reducing the concentration of free and labile metals through cation-exchange.

The data for the 9-14-99 OWC RR water showed that the values of “S” and the pseudo-first order rate coefficient for photobleaching (kOBS) depended on the pH of the solution (Figures 4.2-3). The initial value of “S” at a pH of 8.00 is lower than at a pH of 4.08. At the higher pH, the organic matter will be more deprotonated which results in the absorption to be shifted to higher wavelength (lower energy regions), or red-shifted.
(Schwartzenbach et al., 1993). During the course of the experiment, “S” increased for the sample at both pHs, but the increase was not as severe as what was observed for the pH 4.08 sample. Also, the data were more scattered at the higher pH which suggests that after the initial induction of the photochemistry, the rate of turnover for the lower energy absorbers (the higher molecular weight CDOM fraction) is closer to that for the higher energy absorbers (lower molecular weight CDOM fraction).

At both pHs the value of “S” was found to increase during the course of the reaction and indicated that the CDOM was undergoing a shift in chromophores in the relative proportion of UVB to UVA absorbers. Either the UVA absorbers are being degraded much faster than the UVB absorbers or are being transformed into new UVB absorbers at a faster rate than the photodegradation rate of the UVB absorbers leading to a rise in “S”. Again, this would be consistent the idea that as the CDOM is photolyzed, lower molecular weight material that is more oxidized in nature is being produced.

For the absorbance degradation data, a higher rate coefficient for photobleaching ($k_{OBS}$) was observed at the lower pH compared to the higher pH. If photobleaching occurred as a result of the direct photolysis of the CDOM, I would have expected the opposite trend because the molar absorptivity of the water is higher at the higher pH, indicating that the water more efficiently absorbs light at a higher pH (Table 3.2). Because this trend was not observed I believe that the CDOM photobleaching results from a secondary process where the efficiency of the degradation will be dependent on the solution conditions. For example, a non-NOM source could be generating the
reactive intermediates that are oxidizing the organic material in this raw water sample in a mechanism that is activated at a lower pH.

The data also suggests that $k_{\text{OBS}}$ for photobleaching is wavelength dependent (Figure 4.3). Considering the pH 4.08 sample, the curve increases slightly from 290-320 nm, suggesting a broad peak. At the longer wavelengths, the curve flattens which suggests wavelength independence. For the sample at a pH of 8.00, a broad peak is again observed with a maximum at 340 nm which tapers in the region from 340-400 nm, then drops-off considerably. This suggests that photobleaching at the higher pH is more dependent on wavelength than that occurring at the lower pH. The observation of more featureless $k_{\text{OBS}}$ vs. $\lambda$ curve at the lower pH is consistent with the idea that the pH dependency of the photobleaching of the CDOM in the raw water is caused predominantly at a higher pH by direct photolysis whereas at a lower pH by a secondary CDOM degradation mechanism.

Perturbing the system by adding different scavengers and changing reaction conditions provides additional information in support of these conclusions. Methanol is a good scavenger to add because it does not absorb light in the solar spectrum and therefore, will not interfere with the measured UV/VIS scan or compete with CDOM for photons. The overlay of the UV/VIS scans of solutions with and without MeOH did not differ significantly (Section 3.3.3). The addition of methanol (MeOH) to the pH adjusted OWC 9-14-99 RR sample completely quenched the degradation of alachlor (Section 3.3.3). The addition of MeOH to this sample resulted in a decrease of $k_{\text{OBS}}$ to values reported for the pH = 8.0 sample. The "S" factor remained relatively constant for the first
few hours of the experiment and then gradually increased toward the end of the experiments demonstrating that the CDOM was changing. I would expect the presence of MeOH to quench HO•, while allowing direct photochemical process to occur. Thus, the addition of MeOH should provide a qualitative assessment on how important secondary reactive intermediates are in photobleaching the CDOM. In general, however, “S” for the solution containing MeOH was always lower than corresponding solution (no MeOH at the same pH). If the primary role of the MeOH is to scavenge the HO•, then the diminution of the “S” value from the non-MeOH containing solution indicates the extent that HO• may influence the oxidation and turnover of the CDOM.

The rate coefficient for photobleaching better supports these hypotheses (Figure 4.3). The addition of MeOH results in quenching almost 39 ± 5 % of the photobleaching. More significantly, the k_{OBS} vs. \lambda plot for the MeOH solution very closely corresponds to that obtained for the pH of 8.00 solution, similar to what was observed for the “S” data. Thus, the addition of MeOH indicates that secondary processes leading to CDOM transformation are significant at a low pH, but relatively insignificant at the higher pH. Measuring k_{OBS} in a solution with a pH of 8.00 with MeOH added is strongly suggested to confirm this finding. These results can be used to interpret the results from the alachlor degradation studies in the same samples. While alachlor degradation was completely quenched when MeOH was added to the pH adjusted (4) OWC 9-14-99 RR water, it had less dramatic effect on the photobleaching. The lack of correspondence between results from the two experiments suggests that the alachlor degradation is promoted by the
photochemistry of another process that is either NOT related or only indirectly related to
the CDOM photobleaching.

Furthermore, the pH adjusted (4.14) solution that had been argon sparged was also
analyzed for photobleaching. In the experiment with alachlor, argon sparging of the pH
adjusted OWC 9-14-99 RR solution inhibited alachlor’s degradation by 39%. The \( k_{\text{OBS}} \)’s
for photobleaching were the lowest observed for all solutions tested and in general,
decreased with an increase in the wavelength (Figure 4.3). This behavior suggested that
the UVA to near-UV absorbers (absorbance > 320 nm) were more susceptible to reaction
with oxygen and that \( \text{HO}^* \) may not be the only important transient. When the oxygen in
solution is minimized, the photobleaching of these groups diminishes. On average, argon
sparging reduced \( k_{\text{OBS}} \) for the CDOM photobleaching in this water (9-14-99 RR) by 68
\( \pm 0.09 \) %. That alachlor degradation and photobleaching were significantly inhibited by
argon sparging indicates that ROS are important in mediating both processes. Oxygen
can react with excited state CDOM to form a host of reactive transients (see Section 1.2).
In conditions of minimum \( \text{O}_2 \), the influence of any oxygen mediated pathway should be
effectively reduced (i.e., those involving \( \text{H}_2\text{O}_2, \text{O}_2^*; \text{ROO}^*, \text{HO}^* \) or \( \text{^1O}_2 \)). In addition, if
the photobleaching occurred through a channel involving CDOM triplets, then I would
have expected a promotion of the \( k_{\text{OBS}} \). Similar to the alachlor data, a promotion was not
observed and further supports the idea that CDOM triplets are not important in this
system.

The plot of the “S” values versus irradiation time obtained for argon-sparged
OWC 9-14-99 RR solution showed a very interesting trend (Figure 4.2): it was the only
plot where “S” decreased during the course of the experiment. This trend would be expected because argon sparging diminishes the available supply of oxygen that could be incorporated into the CDOM from photochemically induced oxidation reactions. Thus, these results validate the idea that an increase in UVB absorbance is due to the incorporation of oxygen into the CDOM. When oxygen is prevented from being incorporated into the CDOM matrix, then, the UVB absorbers are disappearing at a faster rate than the UVA absorbers. An explanation for this effect that would be consistent with the data in that the UVA absorbers are more susceptible to degradation from pathways that involve oxygen.

While the photobleaching for the UVB absorbers was also inhibited in the oxygen deficient conditions, it still degraded with a faster rate coefficient relative to the UVA/near-UV absorbers. In the shorter wavelength regions sufficient energy exists to break covalent bonds in the NOM matrix. After a wavelength of about 345nm, there is insufficient energy for the homolysis of C-C bonds, the weakest bonds of bonds that can be photolyzed from the NOM. The ability to homolyze C-O bonds is lost after 332nm, and the ability to homolyze N-H bonds is lost after 307 nm. In the longer wavelength region, absorbed energies are not sufficient to induce bond homolysis, and therefore, would make reaction with reactive transients more important than direct photolysis in their photobleaching. Vaughan and Blough (1998) noted that the highest quantum yield for production of HO• directly from photolysis of CDOM occurred at 320nm and corresponds to the homolysis energy of C-O bonds their observation may suggest a
potential mechanism for the ejection of these very reactive species from the CDOM matrix.

Photobleaching was also measured in cation-exchanged samples of OWC 9-14-99 RR water. At the start of the reaction, the measured “S” value was identical to the raw water. During the course of the experiment, “S” increased to a greater extent than the raw water and was the highest measured of all the solutions. For $k_{OBS}$’s, no significant difference was observed between the plots of the pH adjusted raw water and the proton saturated sample. The “S” trend indicated that the role of free and labile metals was to impede the phototransformation of the CDOM while the degradation data suggests there was no measurable effect of free or labile metals on the photobleaching. However, it is difficult to make an interpretation of the data because a fraction of the CDOM was lost to the cation exchange resin. This loss may have preferentially removed a reactive NOM fraction. Also, without a measure of the error on the “S” determination, it is impossible to comment on the significance of the difference between the two plots.

4.3.2 The Effect of TOC on Photobleaching

Photobleaching was studied in reconstituted OWC XAD-8 isolate solutions to determine if there was a TOC dependency. All solutions were buffered with a phosphate buffer (5 mM) to a pH of 4.1 (Table 3.3). An advantage of studying this system is to gain an understanding of how NOM isolate behaves photochemically in the absence of significant interference from other water constituents (e.g., nitrate, nitrite, or iron).
The determined slopes (except for the 2 mgC/L sample) of absorption curves generally increased with time of reaction (Figure 4.4) and indicated that the longer wavelength absorbers of the OWC XAD-8 NOM are being degraded at a faster rate than the shorter wavelength absorbers during the course of the experiments. Also, (except for curves for the 2.20 and 9.20 mgC/L samples) curves for all concentrations of TOC closely overlap, until the final hours of the experiment. At that point, the value of “S” increases with a corresponding increase in the TOC from 2.26 to 9.20 mgC/L. The similarity of the “S” values at the early time periods would be expected because the molar absorptivities measured at 280 nm for these samples varied little (RSD 3.1%) (Table 3.3) and, therefore, the light absorbing properties for these solutions were expected to be similar. It is not understood why the “S” for the 13.08 mgC/L sample is depressed compared to the other higher TOC samples; although, perhaps it is a result of light screening in the higher TOC sample.

If the photobleaching reaction is truly first order with respect to the TOC, then the photobleaching should result in a \( k_{OBS} \) that is independent of the TOC concentration at a given pH. If the rate coefficient for the reaction is dependent on the TOC, then the photobleaching caused by some other second order process can be approximated for a given solution by pseudo-first order kinetics. The data for the calculated “S” suggested that the latter may be what is occurring since since \( k_{OBS} \) increased with an increase in TOC from 2.26 to 9.20 mgC/L (Figure 4.5). This finding is consistent with the trends observed in “S” for this sample. The rate coefficient measured at any wavelength, however, dropped off considerably for the 13.08 mgC/L. It should be noted that the
$k_{\text{OBS}}$'s for this data set were corrected for both variation in light intensity and for inner filter effects. From my "model" of the alachlor degradation rate coefficients (Section 3.3.5), alachlor degradation was promoted up to a point, and then leveled off. The plateau was interpreted to be the point where NOM scavenging dominated the kinetics. Thus, if ROS are involved in the photobleaching process, as I expected based upon the photobleaching data from the OWC 9-14-99 RR sample set, I would have expected measured $k_{\text{OBS}}$ to behave similarly. If the NOM was scavenging more transients (as was seen from the alachlor degradation experiments), then reaction with those transients would further degrade the NOM. An increase in CDOM degradation should result in an increase absorbance lost, and a correspondingly higher $k_{\text{OBS}}$ for photobleaching. When the CDOM reached a level of 13.08 mgC/L, however, $k_{\text{OBS}}$ dropped off considerably. The cause for this is unknown. The curves for the 2.26 and 4.33 mgC/L points virtually overlap. These samples had the highest level of transparency. Therefore, I suspect the difference between the low and high TOC samples results from the inability of the CDOM to generate the reactive species is because of inner filter effects, and my inability to correct for this process.

Photobleaching $k_{\text{OBS}}$'s also increased, in general, with an increase in wavelength (Figure 4.5) which suggested that the lower energy light (UVA and near-UV) absorbers are being degraded faster than the higher energy UV absorbers. This contrasted with the trends found for the natural water sample where no such dependency was observed. Nevertheless, this observation would still be consistent with the interpretation that ROS or reactive intermediates are reacting with this fraction of the CDOM since it does not
absorb light in the regions that induce chemical reaction (< 330 nm). It is not clear to me
whether this wavelength effect suggests that near-visible and visible regions of light are
causing more turnover than the UV absorption, though, I suppose this could also be an
interpretation of the data.

4.3.3 Effect of pH on the Photobleaching of Natural Water and NOM samples

Bruccoleri et al. (1993) pointed out that the quantum yield for the production of
CDOM triplets increased with a decrease in pH and increased with the addition of a
strong electrolyte (KCl). They asserted this phenomenon occurred because of
conformational changes in the CDOM matrix. A decrease in pH results in an NOM with a
collapsed configuration because of protonation. The addition of a high concentration of a
strong electrolyte will have the same effect on NOM structure because of electrostriction.
Although the data from the argon-sparged sample suggested that CDOM triplets were not
involved in the photobleaching process for this system, this study is noteworthy because it
found that photochemical properties of CDOM were dependent on the pH and that
efficiency of certain photophysical phenomena were dependent on the interaction
neighboring chromophores. Moreover, if \(^3\)CDOM is scavenged efficiently by O\(_2\), then at
low pH, I would expect more ROS production and indirect photobleaching. Since I found
that the reaction of alachlor was pH dependent, I hypothesized that if this reaction was
arising from direct photochemical involvement of the CDOM, then the photobleaching of
the same samples would also be pH dependent. Therefore, photobleaching parameters
were measured in the natural water and NOM isolate samples that were used to investigate the dependency on the pH of the degradation of alachlor (Table 3.1 and 3.4). The sample set included: (1) OWC XAD-8; (2) the proton saturated OWC railroad water sampled on September 14, 1999 (9-14-99 OWC H+); (3) Fulton County NOM isolated via ultrafiltration (Fulton Co. UF); and (4) Suwannee River Fulvic Acid (SRFA).

4.3.3.1 OWC XAD-8 Isolate

Photobleaching of OWC XAD-8 was monitored at high (7.12) and low (4.08) pHs (Figure 4.6). The initial value of “S” was lower for the higher pH sample and reflects the red-shift in the absorbance spectrum due to an increase in the pH. The value of “S” increased with irradiation time at both pHs. “S” measured at pH of 4.08 was consistently higher than that measured at pH 7.12 which reflects the red-shift expected to occur in the absorbance spectrum when the pH is increased. Photobleaching $k_{OBS}$’s were higher at a pH of 4.08 than at 7.12 (Figure 4.7). Interestingly, $k_{OBS}$ increased with an increase in wavelength for the lower pH sample while it decreased with an increase in wavelength for the pH 7.12 sample. At a pH 7.12, the $k_{OBS}$ vs. $\lambda$ plot has a broad peak from 325-340 nm and then decreases. The pH 4.08 curve has broad shoulder from 315 to 330 nm but in general, $k_{OBS}$ continued to increase with wavelength. This observation indicates that something other than direct photochemical processes at the lower pH is transforming the lower energy absorbers at a faster rate than the higher energy absorbing fraction. The data for this “purified” OWC NOM isolate is consistent with the observations made for the
OWC raw water and suggests that an external oxidant is important in mediating photobleaching. At the higher pH, however, direct photolysis appears to be more important.

4.3.3.2 H+ OWC RR Isolate

For this water sample, the raw water was treated by a proton-saturated cation exchange column (Section 3.3.3). Therefore, the effect of free and labile metals (including Fe$^{3+}$ and Fe$^{2+}$) on the photobleaching reaction should be minimized. At a pH of 4, there was no measurable effect from proton saturation of the raw water on the photobleaching $k_{\text{OBS}}$ (Figure 4.3). Interestingly, alachlor degradation in this sample changed the least with an alteration in the pH in comparison with other tested samples (Fulton Co. UF and SRFA) (Table 3.5).

For the photobleaching measurements, the value of “S” increased with irradiation time again, demonstrating the shift in the relative light absorbing population (Figure 4.8). The pH 2.16 curve showed the largest change in “S” with time, followed by the data measured at pH 3.04. The “S” data for the other pHs were very similar in measured values through the course of the experiment. The trends in the data correspond to the measured alachlor degradation (Figure 3.17) in which alachlor’s degradation was greatest at the lowest two pHs and leveled-off in solutions ranging from pH 4 to 8. As observed with the OWC XAD-8 sample, the initial values of “S” decreased with an increase of pH, as expected.
The photobleaching $k_{\text{OBS}}$ followed the same trends as the "S" data for the lower wavelengths (< 350 nm) (Figure 4.9). The $k_{\text{OBS}}$ versus $\lambda$ curve at pH 2.16 had the largest $k_{\text{OBS}}$ which decreased in order of increasing pH (except for the pH 5.23 sample). Corresponding to its low $k_{\text{OBS}}$, the pH 5.23 sample also had the lowest measured shift in the spectral data ("S"). Such an event might be expected if there is a change in mechanism for CDOM photobleaching that results from a change in the pH. As the pH increases, CDOM becomes a better light absorber (as evidenced by an increase in the molar absorptivity at 280 and 310 nm presented in Table 3.5). Thus, photobleaching due to direct photolytic processes would be expected to increase as CDOM begins to absorb more light. It is interesting to note that above 350 nm, the rate coefficients for photobleaching merge together for pHs ranging from 3 to 8 (except pH 5.23 point), and the data becomes more scattered. This observation again suggests that photobleaching of the lower energy CDOM absorbers is caused by secondary reactions as opposed to direct photolysis.

4.3.3.3 Fulton Co. Isolate

The water quality data for the Fulton Co. isolate solutions used in this study are presented in Table 3.5. The cause for the extreme scatter in this photobleaching data set is not known (Figure 4.10-11). The initial "S" values do reflect the same pH dependency as observed in the other samples, but over the course of the experiments, the "S" plots no longer obey a pH dependency, except at the lowest pH (Figure 4.10a). Only the sample
at a pH of 2.12 showed a significant increase of "S" with irradiation time. The other samples had fairly flat profiles or decreased with time. I would have expected this result if a secondary photochemical process is generating reactive intermediates, such as HO•, that are relatively unselective to CDOM and irrespective of the functional group with which they react. In that case, all CDOM would have the same probability of reacting.

The solution at a pH 2 had the largest $k_{\text{obs}}$ for photobleaching (Figure 4.11) similar to what was observed for alachlor in these solutions (Figure 3.17). Interestingly, there is little difference in photobleaching either for the "S" or measured $k_{\text{obs}}$ for the solutions with pHs ranging from 3-8. These results are consistent with those reported for the solutions containing the lowest concentrations of OWC XAD-8: The TOC for these experiments was at 3.5 mgC/L, which is the same concentration that showed no effect for the photobleaching parameters in the OWC XAD-8 experiments (Section 4.3.2).

At pH 4, a sample was also run in a solution that had been argon sparged (Figures 4.10b and 4.11b. In the same water sample, alachlor degradation decreased by 40%. Comparison of "S" curves between the pH 4 and the pH 4/Argon sparged solution fails to show any significant differences, although the argon sparged curve was consistently lower than the unaltered sample. I would have expected more of difference between the samples if ROS were dominating the shift of the CDOM absorbers. The plots for the photobleaching $k_{\text{obs}}$, however, showed that argon sparging resulted, on average, in a 39 ± 0.08% reduction in the rate coefficient for photobleaching. This diminution is consistent with the argon sparging data for the OWC 9-14-99 RR raw water, although the effect on photobleaching was as not as extensive as that measured for the raw water (68%
reduction). It is interesting to note that argon sparging resulted in the same magnitude of reduction in photobleaching for this NOM and in alachlor degradation. This suggests that the photochemical pathways involving oxygen may be important (up to 40%) not only for photobleaching but also for contaminant degradation.

4.3.3.4 Suwannee River Fulvic Acid (SRFA)

SRFA isolate was also used to study photobleaching to provide a basis of comparison for the other observations. Measurement of the “S” values for SRFA solution agrees well with what has been reported in the literature (Miller, 1994). Once again, the initial values of “S” follow the expected trend: a decrease in “S” with an increase in pH (Figure 4.12). During the course of the experiment, the “S” curves for pH 4-8 converged and there was no clear trend in the value of “S” with the pH. The sample at a pH 8.02 appears to have a greatest change in “S” with time, except for the sample at a pH 2.03 which did not appear to level-off as much as the other samples. At this low pH, the CDOM phase would be exist as a “coiled” structure and perhaps the location of chromophores within the matrix continues to promote photochemical processes (Bruccoleri et al., 1993). The value of “S” for the sample at a pH 8.02 is the second highest and indicates that the shift in CDOM absorbers is also important at this pH.

The photobleaching curves followed similar trends (Figure 4.13). The pH 2.03 sample had the highest measured $k_{OBS}$ for photobleaching which increased with wavelength. The pH 8 sample had the second highest measured $k_{OBS}$ for photobleaching.
In this case, however, \( k_{\text{OBS}} \) increased with the wavelength until about 350 nm after which it remained relatively constant. The sample showed little difference in \( k_{\text{OBS}} \) in the pH range of 3-7. These trends correspond to the level of iron measured in the different samples (Table 3.5) and may suggest that trace amounts of iron could be influencing the reaction (primarily at the lower pH). The next set of experiments investigated this idea by testing the effect of trace levels of iron (\( \text{Fe}^{3+} \)) on photobleaching.

4.3.4 Influence of Iron on Photobleaching

Small levels of Fe affected alachlor degradation, and the effect was observed as a function of NOM type and amount present (Section 3.3.9). I found that alachlor degraded to a greater extent in SRFA than LFFA NOM in the presence of low levels of iron (< 50 ppb), and that for a given TOC, the \( k_{\text{obs}} \) for alachlor degradation was higher than that for solution containing only iron. As the iron level increased, however, both NOMs quenched the reaction. LFFA quenched the reaction to a greater extent than the SRFA. Because of these differences in alachlor reactivity, photobleaching was measured in these samples to help to delineate the relationship between the NOM and the iron (Figures 4.14-17).

The initial values of “S” showed little variation for each CDOM sample among the varying levels of iron (~ 0-50 ppb) (Figure 4.14-15). The concentration of iron was so low in these experiments that absorption due to the formation of Fe-DOM complexes was undetectable in the UV-VIS absorption spectra. The average value for the LFFA and
SRFA was 0.022 nm$^{-1}$ (RSD = 0.99%, n=6) and 0.017 nm$^{-1}$ (RSD = 0.40%, n=6), respectively. The value determined for the SRFA also agreed well with that reported for the literature for the same sample (Miller, 1994; Green and Blough, 1994). The difference in value of “S” between the two NOMs is significant, and these spectral differences are representative of the difference in the structural components of the NOM. As end-member NOMs (in terms of carbon source), SRFA fulvic acid is more aromatic than LFFA (McKnight et al., 1994) and would be expected to have an absorbance that tails into longer wavelength regions. This would reduce the ratio of UVB to UVA and near-UVA absorbers resulting in a smaller S value for SRFA.

For SRFA, “S” increases with time during the course of the experiments. This differs from literature where “S” was found to decrease (Miller, 1994). Presumably, this difference is due to the length of irradiation time: it was longer in the literature study relative to that used here. The values for “S” at different iron levels remain close at the beginning and then diverge toward the end of the experiment. At the end of the experiment, a clear trend is seen: the value of “S” decreased systematically with an increase in the level of iron. Possible explanations for this observation include: (1) free radicals generated in the presence of iron react unselectively with the CDOM and results in an absorbance decrease across all wavelength regions, (2) the binding of iron to CDOM to form unreactive complexes, and/or (3) the formation of iron precipitates that preferentially sorb aromatic moieties from the NOM (Meier et al., 1999) removing a certain fraction of the UVB absorbing pool from solution.
The data for the LFFA also shows an increase in “S” with time. The curve with the smallest change is again the sample that contains the highest level of iron (~ 50ppb), reflecting a trend seen with SRFA. During the course of the experiment, there is less distinction of the “S” plots than what was observed for the SRFA and the data is more scattered. Nevertheless, by the end of the experiment, there is also the general trend that the value of “S” decreases with an increase in iron. Because differences between the LFFA samples are less distinct, this suggests that iron interacts to a lesser extent with the LFFA than for the SRFA. If this interaction is responsible for the alachlor degradation, then it may explain why alachlor degradation is more inhibited in the LFFA solutions than in the SRFA solution. The fact that LFFA is less aromatic than the SRFA (Table 3.6) suggests that the differences observed in the reactivity between the two NOMs may indeed be due in part to the selective removal of aromatic moieties from the NOM by sorption to iron surfaces. The difference may also be due to LFFA having a lower molar absorptivity than the SRFA acid solution (Table 3.9). Because LFFA has fewer chromophores than the SRFA, photobleaching is less likely to occur. Overall, the level of iron affected the photobleaching of the CDOM in these samples. It seems to occur to a lesser degree in the LFFA samples than the SRFA. White (2000) found that SRFA in comparison with LFFA produced more HO• which would indicate that the SRFA has the potential to be much more photochemically reactive than the LFFA. In White’s experiments, however, SRFA also contained 5.76ppb Fe compared to 0.62 ppb Fe for the LFFA sample.
For SRFA, $k_{OBS}$ for photobleaching increased with an increase in Fe level (Figure 4.16) and supports the theory that iron produces radicals that unselectively react with the CDOM. The data, however, was clustered in 3 distinct groups: 1.) 0-8 ppb Fe; 2.) 13-23 ppb Fe, 33-53 ppb Fe. In general, the $k_{OBS}$ for photobleaching increased with an increase in wavelength until 330 nm where there was a noticeably broad peak. After 330 nm, $k_{OBS}$ decreased with wavelength. When methanol was added as a scavenger, the photobleaching of the SRFA was inhibited by a factor of ~28% at all wavelengths. The UV/VIS absorption spectrum of the methanol/SRFA solution did not differ significantly from the SRFA solution and thus, methanol addition did not compete for photons.

The photobleaching $k_{OBS}$ for the LFFA NOM did not show any significant trends between the samples tested (Figure 4.17). A broad peak was again apparent around 330 nm. The $k_{OBS}$ decreased with wavelength until ~380 nm where it began to increase again and was unlike that for the SRFA in which $k_{OBS}$ gradually tailed-off. This is a significant difference in the $k_{OBS}$ profiles between the two samples. For LFFA, the longer wavelength absorbers undergo a fast photobleaching. In addition, the photobleaching rate coefficient was generally larger for the LFFA samples than for the SRFA sample, especially at the longer wavelengths. I would have expected the opposite trend based upon the “S” data and the lower molar absorptivity of the LFFA. When MeOH was added to the 0ppb Fe sample, the inhibition was never more than 17% which occurred at 335 nm. At higher wavelengths, there was no apparent inhibition of the photobleaching due to MeOH. Thus, the addition of methanol did not significantly affect the
photobleaching rate of LFFA even though it completely quenched the alachlor reaction in this solution.

4.3.5 Photobleaching Data and Relationship to Contaminant Degradation

For all samples, there was a dramatic drop in the absorbance after the first sampling point (T = 2 hours) than what is observed between sampling times for the remainder of the experiment (even though there is more time between later sampling points) (Figure 4.18). This event occurred at all measured wavelengths, although the effect was more extreme at smaller wavelengths. The initial decrease in absorbance indicated that there is an extremely photochemically labile fraction of the CDOM. The large initial drop was the cause for the lower correlation coefficients in the determination of the photobleaching kOBS. When photobleaching parameters are measured on longer timescales (> 24 hours), the “weight” of the initial drop on the data set will decrease and probably accounts for the reported good fits to the first-order decay model for absorbance degradation (Gao and Zepp, 1998).

A major trend of all samples (except the argon-sparged samples) was that the value of “S” increased with irradiation time. This result differs from the results of several studies (Gao and Zepp, 1998; Whitehead et al., 2000) and this finding, again can be explained when consideration is given to the experimental timescale. Other studies have generally considered experiments conducted on timescales greater than 24 hours (Gao and Zepp, 1998). Experiments that are conducted on similar timescales as this study
(Whitehead et al., 2000) show an increase in calculated “S”. Thus, these results suggest that on a small timescale, photochemical reactions will shift the relative population CDOM from longer wavelength (UVA/near UVA absorbers) to shorter wavelength absorbers (UVB). On a longer timescale, as the fraction of the CDOM containing UVA and near-UVA absorbers is decreased, the rate of addition to the UVB fraction is much less than the rate of degradation of the UVB pool, and subsequently, the values of “S” diminish. Chemically, this event would indicate that the CDOM is being mineralized (i.e., loss of organic carbon as CO₂) on longer timescales. The fact that photobleaching rate coefficients measured for the longer wavelengths were higher than that for the shorter wavelengths also supports this theory. Thus, this study shows that when reporting “S” factors in photochemical studies for near-surface or surface water samples, it is very important to distinguish how long samples have been irradiated or exposed to sunlight prior sampling.

The TOC was found to have a varying effect on photobleaching rate coefficients (Figure 4.19). At low concentrations (< 5 mgC/L) of TOC, photobleaching was independent of the concentration. At higher concentrations (between ~5 and ~13 mgC/L), photobleaching increased, and at the highest TOC (~ 13 mgC/L), photobleaching was depressed. The data were plotted corresponding to several wavelengths, and it appears that photobleaching is more sensitive to changes in TOC at the longer wavelengths (Figure 4.19). Corrections for the variation in light intensity and for inner filter effects failed to account for these differences and indicated that the mechanism by which CDOM is reacting is complicated and probably involves several pathways.
The data was consistent with the idea that NOM acts as both a promoter and scavenger of reactive intermediates. When the photobleaching data was plotted against the rate coefficients measured for alachlor degradation in the same solutions (Figure 4.20), reasonable correlations were obtained ($R^2$'s ranging from 0.76–0.86). Thus, alachlor degradation was correlated to photobleaching in these solutions. The slopes of these correlations quantify the relative sensitivity to changes in $k_{obs}$ (for alachlor degradation) with changes in $k_{OBS}$ (for photobleaching). The slopes decreased with an increase in wavelength, i.e., $\lambda_{290\text{nm}}$ (1.49) < $\lambda_{300\text{nm}}$ (1.43) < $\lambda_{320\text{nm}}$ (1.32) < $\lambda_{350\text{nm}}$ (1.16) < $\lambda_{400\text{nm}}$ (1.01), and suggested that alachlor degradation was less sensitive to changes in photobleaching at longer wavelengths than for shorter wavelengths. The high sensitivity of alachlor degradation to UVB photobleaching may indicate that photochemical reactions resulting in alachlor degradation are promoted to a greater extent by the UVB absorbing fraction of the CDOM. It is interesting that the plots for the higher wavelengths overlay, and the slope approaches a value of one. In this region, both $k_{obs}$ and $k_{OBS}$ change equally and that may indicate that both species are being degraded by the same mechanism, i.e., that the higher wavelength absorbing fraction is primarily acting as a scavenger.

4.3.5.1 Changes in pH

Few studies have considered the effect of pH on photobleaching of CDOM. Dissolved inorganic carbon (DIC) is a bulk parameter that quantifies the amount of total
carbonate species, \( i.e., \text{CO}_2 \) (aq), \( \text{HCO}_3^- \), \( \text{CO}_3^{2-} \), present in a water sample and is a reported product of CDOM photooxidation (Miller and Zepp, 1995). DIC production rates have been reported to have a negligible (Miller and Zepp, 1995) and inverse (Gao and Zepp, 1998) relationship to the pH for Suwannee River and Gulf of Mexico water samples, and a Satilla River water sample, respectively. Bertilsson and Tranvik (2000) reported that DIC production was negatively correlated to the pH. Therefore, no consistent pH trends have been reported using DIC as an indicator. In this experiment, the OWC XAD-8 extract differed in both measured "S" coefficients and photobleaching rate coefficients between the two pHs tested (Figures 4.6-7) and also suggested a negative correlation between photobleaching and pH. A systematic study of the changes in photobleaching with pH may reveal the nature of the apparent pH dependency of NOM photoreactivity.

The data provided some consistent trends for the variation of photobleaching in the pH range from \(~2\) to \(~8\) for the freshwater samples and isolates tested \( i.e., \text{SRFA, OWC 9-14-99 RR H+}, \text{Fulton Co.} \). First, the initial value for "S" decreased with an increase in pH (Figures 4.8, 4.10, 4.12), which was expected since the absorbance spectra of NOM underwent a red shift when the pH of the solutions was increased. During irradiation, it appeared that the lowest pH sample has the greatest change in "S" with time. The curves for the other samples tended to converge over the course of the irradiation.

In addition, the lowest pH sample \(~2\) had the highest rate coefficient for photobleaching for the tested samples (Figures 4.21A, 4.22 A, 4.23A). The differences in
photobleaching reactivity, however, diminished significantly for the higher pHs. This corresponded to what was observed in alachlor reactivity. For the SRFA sample, the profile of the plot (Figure 4.21A) was similar to that observed for the iron concentrations measured in these samples (Figure 3.18). When $k_{\text{OBS}}$ for photobleaching was plotted against the total iron for this sample, good correlations ($R^2 > 0.98$ for all samples) were obtained for all wavelengths plotted (Figure 4.21B). This result suggests that the photobleaching of SRFA is related to the amount of iron present. When plotted, the correlations between $k_{\text{obs}}$ for the alachlor degradation and $k_{\text{OBS}}$ for photobleaching were much weaker ($R^2$'s were 0.76, 0.71, 0.67, and 0.74 for $\lambda = 300 \text{ nm}, 320 \text{ nm}, 340 \text{ nm},$ and $400 \text{ nm}$, respectively) (Figure 4.21C) and would be expected if there were a shift in the indirect photolytic processes governing alachlor degradation as the pH is changed.

Similar plots were constructed from data for the OWC 9-14-99 RR H+ and the Fulton Co. water samples (Figures 4.22, 4.23). Interestingly, the 99-14-99 H+ sample showed no distinct trends and the photobleaching $k_{\text{OBS}}$ was poorly correlated ($R^2$'s < 0.47) with either the total iron or $k_{\text{obs}}$. For the Fulton Co. water, which had the highest levels of iron (~ 40 ppb), $k_{\text{OBS}}$ for photobleaching showed no correlation to the iron, but did correlate to $k_{\text{obs}}$ for alachlor degradation for the selected wavelengths ($R^2$'s were 0.88, 0.83, 0.78 for $\lambda = 300 \text{ nm}, 320 \text{ nm}, 400 \text{ nm}$, respectively) (Figure 4.23B,C).

The pH trends showed that in general, photobleaching decreased as the pH was increased. A possible explanation for the behavior is that the efficiency of photobleaching may be dependent on the conformation of the NOM. Bruccoleri et al. (1993) made the argument that chromophore interactions offered alternate pathways for intersystem
crossing to explain the increase in quantum yield for the production of dissolved NOM triplets with decreasing pH or an increase in ionic strength. NOM tends to coil at lower pHs due to the protonation of acidic functional groups and causes reactive chromophores to be closer in proximity to other functional groups (e.g., an intramolecular hydrogen abstraction from an NOM chain by an excited state carbonyl). At a higher pH, NOM adopts a more extended conformation due to charge repulsion of deprotonated groups and the polar solvent's ability to solvate the negatively charged species. Thus, the reactive chromophores are farther away from functional groups and this distance may be enough to inhibit physically the intramolecular photobleaching reactions from occurring.

It is not clear from this data whether one can delineate the role of NOM and iron in their effect on alachlor degradation. For the SRFA, iron was related to the photobleaching but the weaker correlation between photobleaching and alachlor degradation did not provide strong evidence to link either iron with alachlor degradation. For those samples where photobleaching correlated with alachlor degradation (Fulton Co., SRFA), a stronger relationship at the lower wavelengths was observed. This indicated that UVB chromophores may be driving the degradation process, although the nature of these chromophores (whether they are organic only or NOM-Fe complexes) cannot be ascertained from the data. Interestingly, the Fulton Co. water, which had the highest measured level of iron, did not have a correspondingly higher level of photobleaching. Even though the water differed greatly in composition, the rate coefficients for photobleaching were the same order of magnitude. This may suggest that iron, at this level, had little effect on photobleaching. However, the role of iron remains
unclear in light of the SRFA results. Therefore, a systematic investigation of the effects of iron (at the levels measured in these samples) was undertaken.

4.3.5.2 Effects of Iron on Photobleaching

Bertilsson and Tranvik (2000) reported that high concentrations (> 300 ppb) of iron promoted the photochemical production of DIC from several lake water samples and indicated that iron may facilitate photobleaching through the iron photoredox cycle. The influence of low iron levels (< 50 ppb or < 0.9 µM) on two types of NOM isolates, SRFA and LFFA, was undertaken in this study. Irradiated solutions were buffered (5 mM phosphate) at a pH of 3.6. The results from these reactions provides a “bracket” to classify the importance of iron promoted reactions at the same pH for a range of NOMs that fall between these end members.

In general, photobleaching rate coefficients were higher in the LFFA than in SRFA solutions. However, for SRFA, as the iron level increased, the $k_{obs}$ for photobleaching also increased (Figure 4.24). The correlations, however, become progressively weaker as the wavelength monitored for photobleaching increased (order of $R^2$: 0.90$_{300nm}$ > 0.87$_{330nm}$ > 0.76$_{350nm}$ > 0.63$_{400nm}$ > 0.61$_{425nm}$ < 0.22$_{450nm}$). Conversely, for LFFA, there is no distinct trend for Fe level and observed photobleaching (Figure 4.25). Similarly, the photobleaching rate coefficients for SRFA strongly correlated with alachlor degradation rate coefficients (Figure 4.26), while those for LFFA revealed no clear trends (Figure 4.27).
If photobleaching were a result of the direct photolysis of CDOM only, then photobleaching rate coefficients should not depend on the iron level. Likewise, if iron reacting as an iron hydroxide complex contributed significantly to the photobleaching at the levels added to the solutions, then the photobleaching of both NOMs studied should exhibit a similar dependency. Since only SRFA photobleaching had a dependency on the iron level, it can be assumed that this NOM must interact with iron in a photochemically reactive complex to a more significant extent than LFFA (LFFA photobleaching was independent of iron level). As “end member” NOM, the primary difference in their composition is the higher aromatic content for SRFA than the microbially derived LFFA (31.4% to 15.8%) (McKnight, 1994). The contribution to the aromaticity comes from lignin which degrades to a limited extent to form numerous types of polyphenols, benzaldehydes, benzoic acids, and quinones, which are all capable of binding iron. Since the correlations obtained for photobleaching and iron level were stronger for the UVB chromophores (previous studies have shown that absorbances measured at \( \lambda = 272 \text{ nm} \) (Traina et al., 1990) and \( \lambda = 280 \text{ nm} \) (Chin et al., 1994) correspond to aromatic functional groups), provides evidence that the photochemistry of these groups are an important contributor to the photobleaching.

This photobleaching data can provide some more insight into the relationship between alachlor degradation, iron level, and NOM level. Recall that LFFA dampened alachlor degradation to a greater extent than did the SRFA sample (Figure 3.23). If LFFA binds \( \text{Fe}^{3+} \) to form photochemically unreactive complexes, this may decrease its ability to produce reactive intermediates as a “free species” and would cut-off this pathway from...
occurring in the NOM solutions. Although SRFA-Fe complexes would also inhibit an iron-hydroxide photolysis pathway, they could contribute to iron cycling (and Fenton chemistry) via their own photoreactivity. This pathway, however, must not be as efficient as the iron-hydroxide photolysis since it leads to a dampening of the alachlor degradation at the higher iron concentrations (Figure 3.23).

4.4 Conclusions

Short term irradiation (~24 hours) of CDOM resulted in a shift in the population of chromophores from a lower to higher ratio of UVB to UVA and near UVA absorbers. Photobleaching resulted from both direct and indirect photolytic processes. Although the rate coefficients measured for photobleaching were similar for all solutions studied, their magnitudes were affected by solution composition. Inhibition of photobleaching by argon sparging demonstrated the importance of oxygen in participating in the photobleaching. The photobleaching data confirmed the dual role that NOM plays as both a promoter and scavenger of reactive intermediates. The poor correlations obtained between pH and measured photobleaching indicated that certain secondary photochemical processes were participating in these reactions, and that the extent to which these secondary reactions can influence the photobleaching is dependent on the pH of the solution. Finally, the extent to which iron influenced the photobleaching depended on the composition of the NOM.
$S = 0.9999x + 0.0000$  
$R^2 = 1.0000$

Calculated "S" (nm$^{-1}$) via manual analysis

Figure 4.1: Validation of the computer code.
Figure 4.2: Variation of the slope ("S") of the absorption coefficient as a function of irradiation time for altered OWC RR 9-14-99 water.

Figure 4.3: Pseudo-first order rate coefficients (decrease of absorption coefficients (m\(^{-1}\)) with irradiation time) measured for the photobleaching of Old Woman Creek Water sampled from the railroad site on 9-14-99 in the wavelength range from 290 to 450 nm.
Figure 4.4: Variation of “S” as a function of irradiation time for solutions with various concentrations (mgC/L) of OWC XAD-8 NOM isolate.

Figure 4.5: Wavelength variation of $k_{obs}$ for photobleaching of OWC XAD-8 isolate solutions.
Figure 4.6: Variation of calculated “S” as a function of irradiation time observed for the OWC XAD-8 sample at high (7.12) and low (4.08) pH.

Figure 4.7: Wavelength variation of the \( k_{\text{OBS}} \) for photobleaching for OWC XAD-8 sample at high (7.12) and low (4.08) pH.
Figure 4.8: Variation of calculated "S" as a function of irradiation time observed for the OWC RR 9-14-99 H+ water measured at several pHs.

Figure 4.9: Wavelength variation of the k_{obs} for photobleaching for the OWC 9-14-99 RR H+ water sample at several pHs.
Figure 4.10: Variation of calculated “S” as a function of time observed for the Fulton Co. UF isolate solutions measured at several pHs. The lower curve shows the results when a pH 4 solution is sparged with argon.
Figure 4.11: Variation of the photobleaching $k_{obs}$ for Fulton Co. UF in the wavelength range 290-450 nm. The lower curve represents photobleaching rate when a pH 4.08 solution is argon sparged. The inset shows the fraction of photobleaching reduction achieved for all wavelengths in the test range (290-450 nm).
Figure 4.12: Variation of calculated "S" as a function of irradiation time observed for SRFA solutions measured at several pHs.

Figure 4.13: Wavelength variation of the photobleaching $k_{OBS}$ (hr$^{-1}$) for SRFA solutions at several pHs.
Figure 4.14: Change in the calculated “S” during irradiation for SRFA solutions containing various amounts of iron.

Figure 4.15: Change in the calculated “S” during irradiation for LPFA solutions containing various amounts of iron.
Figure 4.16: Change in photobleaching $k_{obs}$ for SRFA solutions containing various amounts of iron.
Figure 4.17: Change in photobleaching $k_{obs}$ for LFFA solutions containing various amounts of iron.
Figure 4.18: Drop in absorbance observed at the 2-hour time point using data from the OWC RR 9-14-99 proton saturated water sample as an example.
Figure 4.19: Relationship between measured DOC (mgC/L) and photobleaching for OWC XAD-8 solutions.
Figure 4.20: Relationship between photobleaching rate coefficient at several wavelengths and the observed rate coefficient ($k_{obs}$) for alachlor degradation measured in an OWC XAD-8 solution (pH 4.08).
Figure 4.21: Relationship between photobleaching rate coefficient at several wavelengths and the pH (A), total iron (B), and the observed rate coefficient (k_{obs}) for alachlor degradation (C) measured in SRFA solution.
Figure 4.22: Relationship between photobleaching rate coefficient at several wavelengths and the pH (A), total iron (B), and the observed rate coefficient ($k_{obs}$) for alachlor degradation (C) measured in OWC RR 9-14-99 H+ water samples.
Figure 4.23: Relationship between photobleaching rate coefficient at several wavelengths and the pH (A), total iron (B), and the observed rate coefficient ($k_{\text{obs}}$) for alachlor degradation (C) measured in Fulton Co. UF isolate.
Figure 4.24: Relationship between photobleaching rate coefficient at several wavelengths and the level of iron added to SRFA solutions (pH 3.60).

Figure 4.25: Relationship between photobleaching rate coefficient at several wavelengths and the level of iron added to LFFA solutions (pH = 3.59).
Figure 4.26: Relationship between photobleaching rate coefficient at several wavelengths and the observed rate coefficient ($k_{obs}$) for alachlor degradation measured in SRFA solutions of varying iron concentrations (pH = 3.6). Data presented for select wavelengths.
Figure 4.27: Relationship between photobleaching rate coefficient at several wavelengths and the observed rate coefficient ($k_{obs}$) for alachlor degradation measured in LFFA solutions of varying iron concentrations ($pH = 3.6$). Data presented for select wavelengths.
CHAPTER 5

CONCLUSIONS

5.1 Summary of Results

Carbaryl. The base-catalyzed elimination reaction and direct photolysis accounted for the majority of the overall transformation of carbaryl in the agricultural wetland waters at their ambient pH. At lower pH's, however, the extent of the transformation attributable to indirect pathways, i.e., in the presence of naturally occurring photosensitizers, increased significantly. Moreover, the photoenhanced degradation at the lower pH's was found to be seasonally and spatially dependent. A close correspondence between nitrate level and observed reaction rate coefficient in the light is observed, i.e., as nitrate decreased through the wetland (inlet to outlet), the measured rate coefficient for the light-promoted disappearance of carbaryl also decreased. Unlike the June samples, little (< 10%) of the indirect degradation observed in the latter season samples could be attributed to nitrate photolysis, and corresponded well to levels of NOM (as measured by the TOC). No strong evidence was found that free or labile-metal species promoted the reactions in the pH adjusted waters.
Alachlor. Alachlor was not susceptible to degradation from either direct photolysis or dark reaction pathways. Therefore, alachlor was a good probe to examine the indirect processes promoted by the wetland water constituents and reconstituted NOM isolate solutions. At the high pH, the photochemical degradation of alachlor was significant only in the sample that contained the highest amount of nitrate (OWC 6-29-98 IN). At the lower pH's, however, the observed degradation rate coefficient increased significantly (by 5 to 10 times), and was apparently related to the activation of the photochemical pathways associated with the NOM and possibly Fe-NOM complexes. The rate coefficients measured for the photodegradation of alachlor in reconstituted NOM isolates (cation-exchanged material with very low iron levels) were similar in magnitude to those measured in low nitrate, high TOC natural water samples (OWC 9-14-99 RR) and also showed a pH dependency. Thus, these results suggested that NOM plays a role in promoting the photodegradation. To the best of my knowledge this is the first recorded instance that photochemical degradation processes promoted by NOM exhibited a pH dependency. In addition, low levels of iron (< 50 ppb) were found to promote the degradation of alachlor in the presence and absence of selected NOM isolates. The mechanism for the iron promotion in these solutions, however, could not be assessed from the data.

Chromophoric Natural Organic Matter. Short term irradiation (~ 24 hours) of CDOM resulted in an increase of measured “S” values with time. In general, photobleaching rate coefficients reflected the trends observed in the “S” values.
5.2 Environmental Significance

*Effect of Water Constituents on the Observed Photolysis.* Analysis of the water samples and results from the reactions revealed several constituents that are responsible for the observed indirect photolytic processes: total nitrates (the sum of $\text{NO}_3^-$ and $\text{NO}_2^-$), dissolved natural organic matter (NOM), and organically bound iron. The extent of the observed indirect photolysis pathway due to nitrate depended on the concentration of nitrate and the presence of $\text{HO}^*$ scavengers such as dissolved NOM and carbonate species. Because of the level of TOC measured in these samples, carbonate species are expected to play an insignificant role in scavenging (< 8%). Paradoxically, during low nitrate events (< 50 μM), NOM becomes the principal photosensitizer either through the production of $\text{HO}^*$, $\text{H}_2\text{O}_2$, and/or production of an unidentified transient species. The experiments performed with the NOM isolates (cation-exchanged material) suggests that dissolved metal species or metals associated with the NOM play little role in the promotion.

To the best of my knowledge this study is the first to observe indirect photolytic degradation of a contaminant by naturally occurring nitrate levels in a wetland water. The results suggest that nitrates may play an important part in the indirect photolysis of non-point source pollutants passing through OWC during certain times of the year. The amount of nitrates and nitrites present in wetlands such as OWC will be largely dependent upon the amount of agricultural runoff and municipal inputs into the system and the degree of cycling that occurs by phytoplankton, microorganisms, and higher
plants. Conceivably, nitrates in certain wetlands could be sufficiently high enough to impact contaminant photolysis if other scavengers such as carbonates and NOM concentrations are relatively small (e.g., cranberry bogs in the Northeast).

Probably most interesting was the effect that pH had in influencing the extent of both indirect and direct (for carbaryl) photolysis pathways. Indirect photolytic pathways were found to be more significant in the photodegradation of carbaryl and alachlor in pH-adjusted wetland surface water samples than at the higher pH's. For natural waters and NOM isolates tested, the enhancement by light appears to be related to the activation of a pH-dependent photolytic mechanism involving NOM and/or NOM-Fe complexes. The results showed that iron at trace levels in tested water samples may have an important influence in generating reactive transients that can lead to contaminant degradation. The results suggest that in alkaline (high pH) agricultural wetlands, only nitrate may be important in promoting the photodegradation of non-point source pollutants. The extent that nitrate influences as contaminants degradation will depend on the seasonal compositional cycle of the water passing through the wetland. Conversely, in wetlands with acidic waters (e.g., in Astabula, OH), indirect photolysis promoted by NOM and Fe or NOM-Fe complexes of NPS contaminants would be expected.

It was also interesting to see how the some constituents behave in dual roles. For example, natural organic matter, while inhibiting the photochemical degradation pathway of nitrate, promoted (and inhibited) another light induced degradation pathway for the target compounds studied. Certainly, a delicate balance exists between NOM's role as a photosensitizer and an intermediate scavenger. In addition, while the carbonate alkalinity
inhibited carbaryl’s degradation through the scavenging of reactive intermediates, through pH buffering, it enhanced the direct photolytic degradation.

Short term irradiation (~ 24 hours) of CDOM resulted in a shift in the population of chromophores from a lower to higher ratio of UVB to UVA and near UVA absorbers. Photobleaching resulted from both direct and indirect photolytic processes. Although the rate coefficients measured for photobleaching were similar for all solutions studied, their magnitudes were affected by solution composition. Inhibition of photobleaching by argon sparging demonstrated the importance of oxygen in participating in the photobleaching. The photobleaching data confirmed the dual role that NOM plays as both a promoter and scavenger of reactive intermediates. The poor correlations obtained between pH and measured photobleaching indicated that certain secondary photochemical processes were participating in these reactions, and that the extent to which these secondary reactions can influence the photobleaching is dependent on the pH of the solution. Finally, the extent to which iron influenced the photobleaching depended on the composition of the NOM. Overall, indirect photolysis of the CDOM was found to be an important photobleaching process at low pH while direct photolysis dominated the photobleaching at high pH.

5.3 Future Work

The pH dependency of the indirect photolysis needs further investigation. It is still not clear from this work whether the pH dependency is due solely to NOM, or, to the presence of trace metals catalyzing the process. It would be ideal to develop an
experimental plan that would generate a 3-D surface of the pH versus iron versus some third parameter that measures changes in the light promoted reactivity as a result of changes in the first two parameters. A good choice would be to use a molecular probe that is specific to the process promoted by these variables. The theory that hydroxyl radicals are the primary reactive transient involved in these reactions should be further confirmed by the use of hydroxyl radical specific probes. Most studies using the probe technique have not considered in detail the effect that pH, TOC, or trace iron have on measured production rates from NOM. Alachlor may also be a good choice for a probe because of its recalcitrant nature; however, it should be tested for its potential to bind iron.

Furthermore, the effect of other variables on the reactions need to be considered. I suggested that the pH effect may be due to changes in the NOM conformation. Studying the reactions in solutions of varying ionic strength composition would provide further evidence for the validity of this interpretation. Increasing the ionic strength of solutions at a higher pH should have a similar effect on the NOM conformation as lowering the pH. If the proximity of NOM functional groups are necessary for the reactivity, such an experiment would provide further evidence supporting this theory. Additionally, it would be interesting to examine how the measured rate coefficients of degradation differ when concentrations of alachlor are varied. Recently it has been shown that first order degradation of certain compounds changed depending on the initial concentration of the substrate (Canonica, 2001). This effect was attributed to the opportunity that transients of variant lifetimes generated from NOM photolysis would have to react with the substrate.
Finally, this research provided evidence that agricultural contaminant degradation could be promoted in wetland surface waters under the right conditions (high nitrate for the high pH wetland waters or high NOM and Fe levels for acidic wetland waters). However, it is very difficult to extrapolate the laboratory data to what would happen in the field. In order to address this shortcoming, future work needs to incorporate *in situ* field studies to truly evaluate how important these processes will be. First, the seasonal effect of water composition on contaminant degradation must be systematically studied in the other agricultural wetland waters. This work must address what the cycle is for nitrate and contaminant pulses that pass through these wetlands in a given summer season. In addition, studies must be made to assess the basin and hydraulic characteristics that would maximize sunlight penetration and the time for reaction before discharge into the receiving waters. Only in a natural setting can true evaluation be made of the extent that sunlight promoted processes will aid in improving the quality of wetland surfaces waters draining an agricultural watershed.


Barcelo, D. et al. (1995) : This paper presents the exact same data set for Alachlor and Bentazon as the above paper. Nothing new is gained.


Cabaniss S.E. (1992) "Synchronous fluorescence spectra of metal-fulvic acid complexes", Environmental Science and Technology, 26: 1133


Direct photolysis of H2O2 produces HO2. This reaction proceeds with high quantum efficiency. H2O2 has low molar absorptivity (ε = 19.61 M⁻¹ cm⁻¹); therefore, renders it susceptible to inner-filter effects from absorbing compounds in solution; H2O2 does not absorb above ~320nm.


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295


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300


APPENDIX A

ABSORBANCE SPECTRA AND KINETIC TIMECOURSES FOR THE CARBARYL STUDY

A.1 UV-VIS Spectra of Natural Waters

Figure A.1: UV/VIS for OWC water samples collected on 6-29-98.
September Inlet (pH=7.8)
September Railroad (pH=8.0)
September Outlet (pH=7.7)
August Railroad (pH=7.9)

Figure A.2: UV/VIS for OWC water samples collected on 9-14-99

Figure A.3: UV/VIS for OWC Inlet 6-29-98 at high (~8) and low (~4) pH.
Figure A.4: UV/VIS for OWC RR 6-29-98 at high (~8) and low (~4) pH.

Figure A.5: UV/VIS for OWC OUT 6-29-98 at high (~8) and low (~4) pH.
Figure A.6: UV/VIS for OWC AUG RR at high (~8) and low (~4) pH.

Figure A.7: UV/VIS for OWC IN 9-8-98 at high (~8) and low (~4) pH.
Figure A.8: UV/VIS for OWC RR 9-8-98 at high (~8) and low (~4) pH.

Figure A.9: UV/VIS for OWC OUT 9-8-98 at high (~8) and low (~4) pH.
Figure A.10: UV/VIS for pH adjusted and proton saturated OWC IN 6-29-98 sample.
A.2 Kinetic Timecourses

Figure A.11: Photoinduced degradation of carbaryl in OWC IN 6-29-98 water sample.

Figure A.12: Photoinduced degradation of carbaryl in OWC RR 6-29-98 water sample.
Figure A.13: Photoinduced degradation of carbaryl in OWC OUT 6-29-98 water sample.

Figure A.14: Photoinduced degradation of carbaryl in OWC RR 8-24-98 water sample.
Figure A.15: Photoinduced degradation of carbaryl in OWC IN 9-8-98 water sample.

Figure A.16: Photoinduced degradation of carbaryl in OWC RR 9-8-98 water sample.
Figure A.17: Photoinduced degradation of carbaryl in OWC OUT 9-8-98 water sample.

Figure A.18: Photoinduced degradation of carbaryl in pH 8.00 borate buffer (10mM).
Figure A.19: Photoinduced degradation of carbaryl in pH 7.98 carbonate buffer (2 mM).

Figure A.20: Photoinduced degradation of carbaryl in OWC IN 6-29-98 pH adjusted water sample.
Figure A.21: Photoinduced degradation of carbaryl in OWC RR 6-29-98 pH adjusted water sample.

Figure A.22: Photoinduced degradation of carbaryl in OWC OUT 6-29-98 pH adjusted water sample.
Figure A.23: Photoinduced degradation of carbaryl in OWC IN 6-29-98 pH adjusted water sample that was proton saturated.

Figure A.24: Photoinduced degradation of carbaryl in OWC RR 8-24-98 pH adjusted water sample.
Figure A.25: Photoinduced degradation of carbaryl in OWC RR 8-24-98 pH adjusted water sample with nitrate (1 mM) spike.

Figure A.26: Photoinduced degradation of carbaryl in OWC IN 9-8-98 pH adjusted water sample.
Figure A.27: Photoinduced degradation of carbaryl in OWC RR 9-8-98 pH adjusted water sample.

Figure A.28: Photoinduced degradation of carbaryl in OWC OUT 9-8-98 pH adjusted water sample.
Figure A.29: Photoinduced degradation of carbaryl in pH 4.35 phosphate buffer (5 mM).

Figure A.30: Photoinduced degradation of carbaryl in pH 4.35 buffered XAD-8 solution.
Figure A.31: Photoinduced degradation of carbaryl in pH 4.35 buffered XAD-4 solution.
APPENDIX B

ABSORBANCE SPECTRA AND KINETIC TIMECOURSES FOR THE ALACHLOR STUDY

B.1 UV-VIS Spectra of Natural Waters

Figure B.1: UV/VIS for OWC 6-29-98 Inlet water at low and high pH.
Figure B.2 UV/VIS for OWC 9-14-99 Railroad water at low and high pH.

Figure B.3: UV/VIS of OWC 9-8-98 Outlet water.
Figure B.4: UV/VIS of Suwannee River water (diluted to 5.95 mgC/L).

Figure B.5: UV/VIS of Defiance County wetland water sample at low and high pH.
Figure B.6: UV/VIS of Fulton County wetland water sample.

Figure B.7: UV/VIS spectra of VanWert County wetland water at low and high pH.
Figure B.8: UV/VIS spectra of Champaign County wetland water at low and high.
Figure B.9: Photodegradation of Alachlor in buffered MilliQ water samples at pH 8.08 (a) and 4.21 (b).
Figure B.10: Photoinduced degradation of alachlor in OWC 6-29-98 Inlet water at the natural pH (a) and pH ≈ 2.78 (b).
Figure B.11: Photoinduced Degradation of alachlor in OWC 9-14-99 Railroad water at the natural pH (a) and a pH of 4.08 (b). An experiment performed in argon sparged solution is also presented (b).
Figure B.12: Photoinduced degradation of alachlor in OWC 9-8-98 Outlet water at the natural pH (8.09) of the water.
Figure B.13: Photoinduced degradation of alachlor in the Defiance Co. wetland water. (a) unadjusted pH and (b) pH adjusted water.
Figure B.14: Photoinduced degradation of alachlor in the Fulton Co. wetland water. (a) unadjusted pH and (b) pH adjusted water.
Figure B.15: Photoinduced degradation of alachlor in the VanWert Co. wetland water. (a) unadjusted pH and (b) pH adjusted water.
Figure B.16: Photoinduced degradation of alachlor in the Champaign Co. wetland water. (a) unadjusted pH and (b) pH adjusted water.
Figure B.17: Photoinduced degradation of alachlor in Suwannee River raw water (pH = 4.26)